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ANNUAL TECHNICAL REPORT

Grant No. [REDACTED]

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Principal Investigator:  
Rodney J. Bartlett

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFOSR)

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Binding energies including valence-shell electron correlation were obtained from many-body perturbation theory (MBPT) for diborane, borane carbonyl, and borane. Results were obtained for basis sets of double zeta quality and for basis sets with polarization functions added on all atoms. The binding energies were found to be (respectively) 35, 21, and 30 kcal/mole. Correlation effects account for 48, 62, and 32 percent of the binding. The size-consistent nature of the MBPT method enables the computation of enthalpies of reaction for four different reactions involving monoborane, diborane, carbon monoxide, and borane carbonyl.		

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When the theoretical values are corrected for vibrational zero-point energies and the experimental data are adjusted for temperature effects, the results agree (within 5 percent) and thus confirm the set of experimental enthalpies for the association reaction yielding diborane. The result for the binding energy of borazane constitutes a prediction in the absence of an experimental value.

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Columbus Laboratories

at Kent, Akron

Cincinnati, Ohio 45201

Telephone (614) 424-6100

Telex 14444

September 15, 1980

Dr. Ralph Kelley  
Air Force Office of  
Scientific Research  
Building 410  
Bolling Air Force Base, D. C. 20332

Dear Dr. Kelley:

Re: Grant No. [REDACTED]

*AFOSR-78-3661*

Enclosed are six(6) copies of our Annual Technical Report on the above grant entitled "Molecular Interactions with Many-Body Perturbation Theory."

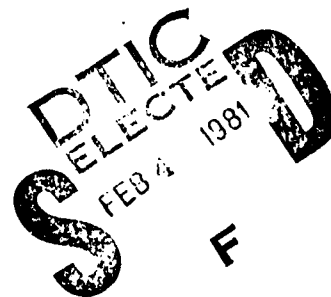
Sincerely,

*Rodney J. Bartlett*

Rodney J. Bartlett  
Physical Sciences Section

RJB/sp

Enc. (6)



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### APPENDIX A

ELECTRON CORRELATION IN LARGE MOLECULES WITH MANY BODY METHODS

### APPENDIX B

THE REDUCED LINEAR EQUATION METHOD IN COUPLED CLUSTER THEORY

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## I. DESCRIPTION OF PROBLEMS

In a wide variety of Air Force applications, highly detailed information about atoms, molecules, and their interactions is required<sup>(1-3)</sup>. This information is necessary in problems ranging from chemical laser development, to the detection and identification of rocket plumes, to metal clustering and aerosol formations, and even to nuclear weapons effects.<sup>(1-3)</sup>

Probably the most crucial component needed to understand molecular reactions is the potential energy surfaces that serve to describe the attractions among the atoms and molecules.<sup>(1)</sup> However, such information is not easy to obtain. A certain amount of information about the molecular forces near equilibrium in a bound molecule is available from spectroscopy. Some information about the potential energy surface even in the absence of binding can be provided from crossed molecular-beam experiments. But, in general, potential energy surfaces are not amenable to experimental determination. Instead, other types of experimental observations such as kinetics experiments, coupled with very simple theoretical models for a surface, are used to infer pieces of information about the parameters of the model such as what the activation barrier might be.

The most direct approach to obtaining detailed information about a potential energy surface is offered by predictive, ab initio quantum mechanical calculations. However, to make it feasible to calculate accurate energy surfaces for molecules, much better and more computationally efficient methods must still be developed.

One such approach, namely many-body perturbation theory (MBPT)<sup>(4-15)</sup> and its infinite-order extensions termed coupled-cluster methods (CCM)<sup>(11,16-20)</sup>

offer a number of attractive features that the more traditional configuration interaction approaches lack.<sup>(21)</sup> During the first two years of this grant very efficient computer codes to perform MBPT/CCM calculations were written and employed for the first time in large-scale ab initio calculations of potential energy surfaces.<sup>(11,21)</sup> The successes of this effort have been substantial. These include the determination of a complete force-field for the H<sub>2</sub>O molecule, including all force-constants through fourth-order, that is sufficiently accurate that once improved experiments were carried out after our calculations, many of the previously accepted values for the force constants were revised to be more consistent with our predictions.<sup>(22)</sup> Also, a study of the binding energies of the molecules B<sub>2</sub>H<sub>6</sub>→2BH<sub>3</sub>, H<sub>3</sub>BNH<sub>3</sub>→BH<sub>3</sub>+NH<sub>3</sub>, and H<sub>3</sub>BCO→BH<sub>3</sub>+CO was made that predict these binding energies to within 1 kcal/mole of the accepted experiments for diborane and borane carbonyl, and made a prediction in the case of borazane in the absence of an experiment.<sup>(14)</sup> Earlier experiments which gave much higher values for the binding energies of diborane and borane carbonyl than we computed are now completely discounted. Similar successes with studies of the isomerization energy and activation barrier of HNC→HCN,<sup>(23)</sup> and CH<sub>3</sub>NC→CH<sub>3</sub>CN,<sup>(24)</sup> the photodissociation of formaldehyde,<sup>(25)</sup> and various studies of methanol, methoxy, and the formyl radical<sup>(26)</sup> attest to the reliability of our MBPT/CCM methods.

Building upon this work supported by the AFOSR we have now carried out extensive studies of the potential energy surface for the two inelastic collisions, O(<sup>3</sup>P)+H<sub>2</sub>O and O(<sup>3</sup>P)+CO<sub>2</sub>, under contract to the Air Force Rocket Propulsion Laboratory, for the purpose of obtaining vibrational excitation cross-sections that are needed in actual detection devices.<sup>(27)</sup>

Despite the many successes we have had, there are still categories of problems that cannot yet be attacked by MBPT/CCM. These include studies of most excited states, reactions that break multiple bonds, and applications to various kinds of open-shell molecules.<sup>(21)</sup> To satisfy these additional requirements it is necessary to simultaneously develop the formal theory, write additional computer programs, and continue to make landmark applications of our developing quantum mechanical technology. Although in many cases the formal theory is less dramatic than the applications, the continual extension of the theory has a greater impact on our ability to calculate accurate energy surfaces for whatever categories of problems might emerge from the needs of the Air Force.

Consistent with this objective, much of our work this past year has been devoted to formal theory. This includes optimization of orbitals within the coupled-cluster framework and developing additional mathematical techniques to efficiently solve the non-linear coupled cluster equations. Additional applications to a variety of problems have also been accomplished.

In the following, Section II discusses the research objectives of this grant, and summarizes some of the notable accomplishments made in the past year. For the previous year's effort, we refer to last year's annual report. Section III lists the publications and presentations which have been supported by this grant. Section IV discusses in some detail the idea of orbital optimization in coupled-cluster theory. This is a radically new approach of substantial scientific interest. Appendices A and B are two manuscripts recently accepted for publication. The first

discusses applications of MBPT/CCM to large molecules, while the second reports on a new mathematical technique we have developed to efficiently solve the non-linear equations of the type that occur in coupled cluster theory.

## II. REVIEW OF RESEARCH ACCOMPLISHMENTS

The overall objectives of this research program include the following:

- (1) Develop new, more accurate and more efficient ab initio quantum mechanical methods based upon MBPT and CCM for determining molecular properties and particularly, potential energy surfaces for molecular interactions.
- (2) Implement these methods in highly efficient, transportable computer codes, to enable computations on potential energy surfaces to be made on an almost routine basis.
- (3) Apply these techniques to a variety of problems that are of interest to AFOSR, and that serve to establish the range of accuracy for MBPT and CCM methods.

In line with these overall objectives, a number of accomplishments have been made so far in this program. The accomplishments from the previous year are listed in the Annual Report for 1979. Hence, we will summarize only the additional achievements that have been made in the past year.

The main focus for our effort this last year has been formal, being directed toward the generalization of the MBPT and CCM theory. In particular, the inclusion of monoexcited clusters and the theory required for orbital optimization have been developed within the CCM model. Additional

formal work has been directed at the multireference MBPT/CCM theory. A series of applications to a wide variety of problems using our previously established computer codes have also been made to demonstrate the applicability of our developing methods. A summary of achievements follows.

- A. The coupled-cluster theory and programs have been generalized to include monoexcited clusters (i.e.,  $T_1$ ). This is found to be important in obtaining correct potential energy curves for cases where a single-determinant reference function is not entirely appropriate.
- B. For the first time, the effect of optimizing the molecular orbitals in the coupled-cluster theory has been studied. This model is similar to a multi-configuration self-consistent field (MCSCF) approach, except, via CCM, one employs all single, double, and quadruple type CI excitations. Nothing of this magnitude has been attempted previously. We are using this method to study some unusually difficult molecular problems.
- C. A new numerical technique,<sup>(28)</sup> similar to the reduced partitioning procedure developed for eigenvalue problems by the author some years ago,<sup>(29)</sup> has been generalized to apply to the nonlinear coupled-cluster

equations. This has the effect of greatly increasing the rate of convergence when solving the equations. This has enabled us to obtain accurate results for some pathological cases that could not have been obtained by the standard iterative approach. (See Appendix B).

- D. The decomposition of formaldehyde,  $\text{H}_2\text{CO}$ , to radical and molecular products and its rearrangement to hydroxycarbene has been studied.<sup>(25)</sup> This problem is of substantial experimental interest because of formaldehyde's prominence in combustion/plume processes. The activation barriers and heats of reactions have been obtained. In the latter case, agreement with experiment is within  $\pm 2$  kcal/mole. The activation barrier predictions support the CI results of Goddard and Schaefer<sup>(30)</sup> that would suggest a tunneling mechanism for  $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$ .
- E. A series of detailed comparisons of various MBPT models with CCD for the C, N, and O atoms and the  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{CH}_4$  molecules were made this year.<sup>(21)</sup> These comparisons, plus a number of others we have made, suggest that the infinite-order CCD results differ insignificantly from the fourth-order model, DQ-MBPT(4), for most normal cases.<sup>(21)</sup> This supports the predictions of the less expensive fourth-order model for larger molecules.

- F. An experimentalist measured the isomerization energy of  $\text{HNC} \rightarrow \text{HCN}$  to be  $10 \pm 1$  kcal/mole.<sup>(31)</sup> This disagreed with our theoretical prediction of  $15 \pm 2$  kcal/mole.<sup>(24)</sup> To attempt to resolve this discrepancy, we performed calculations on this system for a series of approximations and basis sets, concluding, indeed, that the value  $15 \pm 2$  kcal/mole is accurate.<sup>(23)</sup> We believe this will prove to be another case where theory has demonstrated that the experimental value is in error.
- G. In addition to the  $\text{HNC} \rightarrow \text{HCN}$  rearrangement, the interesting systems  $\text{LiNC} \rightarrow \text{LiCN}$  and  $\text{BNC} \rightarrow \text{BCN}$  were also studied.<sup>(23)</sup> Essentially no barrier to rearrangement is found for  $\text{LiNC} \rightarrow \text{LiCN}$ , while  $\text{BNC}$  is found to be more stable than  $\text{BCN}$ . Our calculations made predictions of the thermochemistry parameters for these molecules which we hope will stimulate some experimental work.
- H. The first all-electron ab initio coupled-cluster and MBPT calculations of benzene were made this year. This work demonstrates that a molecule of this size has at least a 20 percent error in its correlation energy due to the neglect of CI type quadruple excitations.<sup>(32)</sup> This emphasizes the importance of using methods like MBPT/CCM that properly include such higher order excitation effects if reliable quantum mechanical calculations are to be possible for larger molecules. (See Appendix A.)

I. Additional calculations at the MBPT/CCM level on a variety of systems including  $\text{Li}_4$ ,  $\text{CH}_3\text{O}$ ,  $\text{HNO}$ , and other unusual molecules are also being made to predict structures, thermochemistry, and other properties like Jahn-Teller distortions.

### III. PRESENTATIONS AND PUBLICATIONS

#### Presentations (1980)

R. J. Bartlett, "Potential Energy Surfaces with Many-Body Methods" invited speaker, Canadian Theoretical Chemistry Conference, June 17, 1980.

R. J. Bartlett, "Many-Body Methods and Their Molecular Applications", invited speaker, New York Academy of Sciences Conference on Quantum Chemistry in the Biomedical Sciences, New York, June 2, 1980.

R. J. Bartlett, "Molecular Applications of Many-Body Perturbation Theory and Coupled Cluster Methods," Argonne National Laboratory, Argonne, IL, January 1980.

R. J. Bartlett, "Molecular Hyperpolarizabilities: Correlated Predictions", Sanibel Symposium on the Quantum Theory of Matter, March 11, 1980.

G. D. Purvis, "Orbital Optimization and Reduced Partitioning Method Within Coupled Cluster Theory", Sanibel Symposium on the Quantum Theory of Matter, March 13, 1980.

Presentations (1979)

R. J. Bartlett, "Molecular Applications of Coupled-Cluster and Many-Body Perturbation Methods", invited talk, Nobel Symposium on Many-Body Theory, Lerum, Sweden, June 11, 1979.

R. J. Bartlett, "Accurate Applications of Correlated Ab Initio Quantum Chemistry to Realistic Chemical Problems", Univ. of Kentucky, Lexington, Ky., February 2, 1979.

R. J. Bartlett, "Coupled-Cluster Theory for Molecular Potential Energy Surfaces", invited speaker, Sanibel Symposium on Quantum Theory of Matter, Palm Coast, Florida, March 12, 1979.

R. J. Bartlett, "Coupled Cluster Theory, Many-Body Perturbation Theory and Their Molecular Applications", Ohio University, Athens, Ohio, May 6, 1979.

R. J. Bartlett, "Have Ab Initio Quantum Mechanical Applications Finally Arrived?", University of Florida, Gainesville, Florida, May 11, 1979.

R. J. Bartlett, "Accurate Applications of Correlated Quantum Chemical Methods to Real Chemical Problems", Mount Sinai School of Medicine, New York, New York, June 4, 1979.

R. J. Bartlett, "Many-Body Perturbation Theory", Aarhus University, Aarhus, Denmark, June 18, 1979.

R. J. Bartlett, "Have Ab Initio Quantum Mechanical Applications Finally Arrived?", University of New Orleans, New Orleans, LA, October 5, 1979.

R. J. Bartlett, "Have Ab Initio Quantum Mechanical Applications Finally Arrived?", Tulane University, New Orleans, LA, October 8, 1979.

R. J. Bartlett, "Have Ab Initio Quantum Mechanical Applications Finally Arrived?", Millsaps College, Jackson, Mississippi, October 10, 1979.

R. J. Bartlett, "Have Ab Initio Quantum Mechanical Applications Finally Arrived?", University of Arkansas, Little Rock, Arkansas, October 12, 1979.

Presentations (1978)

R. J. Bartlett, "Molecular Applications of Many-Body Perturbation Theory", invited talk, American Conference on Theoretical Chemistry, Boulder, Colorado, June 29, 1978.

R. J. Bartlett, "Theoretical Contribution to the Plume Enhancement Problem", invited talk, High Altitude Infra-red Radiation Workshop, Air Force Geophysics Laboratory, Lexington, Massachusetts, August 3, 1978.

R. J. Bartlett, "Beyond Hartree-Fock: Perturbation Theory", invited talk, at the National Resource for Computation in Chemistry Workshop on "A Study of Post Hartree-Fock: Configuration Interaction", Berkeley, California, August 14, 1978.

R. J. Bartlett, "Many-Body Perturbation Theory and Coupled Cluster Methods for Molecules", Department of Applied Mathematics, University of Waterloo, Waterloo, Canada, November 13, 1978.

R. J. Bartlett, "Is Size-Consistency Important in Molecular Calculations?", Introductory Lecture, Sanibel Symposium on the Quantum Theory of Matter, Palm Coast, Florida, March, 1978.

R. J. Bartlett, "Is Size-Consistency Important in Molecular Calculations?", Midwest Theoretical Chemistry Conference, April, 1978.

G. D. Purvis, "Comparison of RHF and UHF Based Correlated Methods for the  $N_2$  Potential Curve", Midwest Theoretical Chemistry Conference, April, 1978.

G. D. Purvis, "Comparison of RHF and UHF Based Correlation Methods for the  $N_2$  Potential Curve", American Conference on Theoretical Chemistry, June 28, 1978.

Publications (1980)

R. J. Bartlett and G. D. Purvis, "Molecular Applications of Coupled Cluster and Many-Body Perturbation Methods", Proceedings of Nobel Symposium on Many-Body Theory, Physica Scripta 21, 255 (1980).

R. J. Bartlett and G. D. Purvis, "Electron Correlation in Large Molecules" in press, Proceedings of New York Academy of Science. (Appendix A)

G. D. Purvis and R. J. Bartlett, "Reduced Linear Equation Method in Coupled Cluster Theory", to be published, J. Chem. Phys. (Appendix B)

L. T. Redmon, G. D. Purvis, and R. J. Bartlett, "Correlation Effects in the Isomeric Cyanides,  $\text{HNC} \leftrightarrow \text{HCN}$ ,  $\text{LiNC} \leftrightarrow \text{LiCN}$ , and  $\text{BNC} \leftrightarrow \text{BCN}$ ", J. Chem. Phys. 72, 986 (1980).

G. Adams, G. Bent, R. J. Bartlett, and G. D. Purvis, III, "Formaldehyde: Electronic Structure Calculations for the  $S_0$  and  $T_1$  States", J. Chem. Phys., in press.

Publications (1979)

R. J. Bartlett, I. Shavitt, and G. D. Purvis, "The Quartic Force Field of  $\text{H}_2\text{O}$  Determined by Many-Body Methods that Include Quadruple Excitation Effects", J. Chem. Phys. 71, 281 (1979).

L. T. Redmon, G. D. Purvis, and R. J. Bartlett, "Accurate Binding Energies of Diborane, Borane Carbonyl, and Borazane Determined by Many-Body Perturbation Theory", J. Am. Chem. Soc. 101, 2856 (1979).

R. J. Bartlett and G. D. Purvis, "Molecular Hyperpolarizabilities I. Theoretical Calculations Including Correlation", Phys. Rev A20, 1313 (1979).

G. Adams, G. Bent, G. D. Purvis, and R. J. Bartlett, "The Electronic Structure of the Formyl Radical,  $\text{HCO}$ ", J. Chem. Phys. 71, 3697 (1979).

G. D. Purvis, and R. J. Bartlett, "The Potential Energy Curve for the  $X^1\Sigma_g^+$  State of  $\text{Mg}_2$  Calculated with Coupled-Pair Many-Electron Theory", J. Chem. Phys. 71, 548 (1979).

Publications (1978)

R. J. Bartlett and G. D. Purvis, "Many-Body Perturbation Theory, Coupled Pair Many-Electron Theory, and the Importance of Quadruple Excitations for the Correlation Problem", *Inter. J. Quantum Chem.* 14, 561 (1978).

J. W. Kenney, J. Simons, G. D. Purvis, and R. J. Bartlett, "Low-Lying Electronic States of Unsaturated Carbenes", *J. Amer. Chem. Soc.* 100, 6930 (1978).

L. T. Redmon, G. D. Purvis, and R. J. Bartlett, "The Unimolecular Isomerization Reaction of Methylisocyanide to Methylcyanide", *J. Chem. Phys.* 69, 5386 (1978).

R. J. Bartlett, "Perturbation Theory", Post-Hartree Fock: Configuration Interaction Workshop, NRCC, LBL-8233 (1978).

G. D. Purvis and R. J. Bartlett, "The Potential Energy Curve for the  $X^1\Sigma_g^+$  State of  $Mg_2$  Calculated with Many-Body Perturbation Theory", *J. Chem. Phys.* 68, 2114 (1978).

#### IV. SYNOPSIS OF ORBITAL OPTIMIZATION IN COUPLED CLUSTER THEORY

A new idea which has been developed over the second year of this grant is the optimization of molecular orbitals while simultaneously carrying out coupled cluster calculations. This approach is similar in philosophy to multi-configuration self-consistent field (MCSCF) theory, but differs substantially in numerous other respects.

The traditional MCSCF approach takes a small number (typically 5-20) configurations which we will designate as  $\{D_k\}$ , composed of a set of molecular orbitals,  $\{x_i\}$ . The wavefunction then takes the form

$$\psi_{\text{MCSCF}} = \sum_k C_k D_k$$

where each  $D_k$  is a determinant (or symmetry adapted combination of determinants) of the general form

$$D_k = A(x_1(1)x_2(2)\dots x_a(i)\dots x_b(j)\dots x_n(n))$$

Various replacements (like  $x_a(i)$  and  $x_b(j)$ ) of molecular orbitals which are occupied in  $D_1$  (often the SCF determinant) give rise to the usual CI single, double, etc. excitations. The linear coefficients  $C_k$  are optimized by using the variational principle in a small CI eigenvalue problem. This is the multi-configuration step. The SCF part occurs when the coefficients  $\{c_u\}$  in the molecular orbitals  $\{x_i\}$ ,

$$x_i = \sum_u c_u \phi_u$$

for  $\phi_u$  some primitive, usually atomic orbital basis set, are also simultaneously optimized. This procedure is particularly useful in types of open-shell

problems, and in descriptions of bond breaking when the form of the molecular orbitals can change significantly.

However, there are a number of disadvantages with the MCSCF method. The small number of configurations have to be carefully chosen if correct answers are to be obtained and this requires a difficult and time consuming trial and error procedure. As a consequence, MCSCF methods have notoriously bad convergence properties.

The most important weakness from our viewpoint pertains to MCSCF's failure to be size-extensive. That is, the calculations do not scale properly with molecular size. This occurs due to the method using a variational CI step, which makes it suffer from the same weakness as any truncated CI, inspite of optimizing the orbitals. MCSCF's failure to be size-extensive causes problems ranging from decreasing its applicability to large molecules to correct predictions of dissociation energies. The various difficulties encountered with nonsize-extensive methods are documented in detail elsewhere.<sup>(11,21)</sup>

Recently, a series of papers have appeared that develop an approach for efficiently optimizing the orbital coefficients,  $\{c_u\}$ , and the CI coefficients  $\{C_k\}$  simultaneously.<sup>(33-35)</sup> This approach exploits an idea due to Levy<sup>(36)</sup> of using, unitary exponential operators to perform the orbital rotation. The same approach can be used within the coupled-cluster framework which will have the advantages; (1) that all results are size-extensive; and (2), that the configuration expansion is not just a few determinants, but consists of all single, double, and (via the nonlinear coupled cluster scheme) the quadruple excitations.

Consider the hamiltonian  $H$ , related to the usual electrostatic hamiltonian by

$$H = U^\dagger H U \quad (1)$$

where  $U$  is a similarity transformation, which we will choose to be unitary. The unitarity can be ensured by defining

$$U = e^{i\eta} = e^\kappa \quad (2)$$

For  $\eta$  a hermitian operator, which makes  $\kappa$  skew hermitian (i.e.,  $\kappa^\dagger = -\kappa$ ),

$$H = e^{-\kappa} H e^\kappa \quad (3)$$

where

$$\kappa = \sum_{r>s} \kappa_{rs} (X_r^\dagger X_s - X_s^\dagger X_r) \quad (4)$$

The eigenvalues of any hamiltonian of the form in Eqs. (1) and (3) are unchanged by the transformation, so this transformed  $H$  may be treated just as the ordinary hamiltonian, although an additional degree of flexibility is introduced by the transformation.

Employing the coupled-cluster ansatz,

$$\begin{aligned} \psi_{CC} &= e^T |\phi_0\rangle \\ T &= T_1 + T_2 + \dots \\ T_n &= 1/n! \sum_{ijk\dots} t_{ijk\dots}^{abc\dots} X_a^\dagger X_b^\dagger X_c^\dagger \dots X_k X_j X_i \end{aligned} \quad (5)$$

for  $\phi_0$  a single determinant reference function and  $\psi_{CC}$  intermediately normalized, we can back-project  $\psi_{CC}$  onto a sufficient set of single, double, etc., excitations to give the CC equations,

$$a_i + \sum_j b_{ij} t_j + \sum_{j,k} c_{ijk} t_j t_k + \sum_{j,k,l} d_{ijkl} t_j t_k t_l \dots = 0 \quad (6)$$

for the various amplitudes  $\{t_i\}$  in the operator  $T$ . The quantities  $a_i$ ,  $b_{ij}$ ,  $c_{ijk}$ , etc. are combinations of integrals relative to the molecular orbital basis set.

If we limit ourselves to  $T=T_2$ , then we obtain the coupled cluster doubles (CCD) model, which terminates Eq. (6) after quadratic terms, and requires that we determine as many amplitudes  $t_k = t_{ij}^{ab}$  as there are distinct double excitations. If we approximate  $T=T_1 + T_2$ , then  $T_1$  will occur to the fourth-power,  $T_2$  quadratically, and the coupling terms  $T_1 T_2$  and  $T_1^2 T_2$  will also contribute. In this case, we have both the single excitation amplitudes,  $t_i^a$ , and double-excitation amplitudes to obtain. The energy is given from the Schrödinger equation by

$$E = \langle \phi_0 | H | \psi_{CC} \rangle = \langle \phi_0 | H e^T | \phi_0 \rangle, \quad (7)$$

$$= \sum_{\substack{i>j \\ a>b}} \langle ij || ab \rangle t_{ij}^{ab} + \sum_{i,a} \langle i | h_1 | a \rangle t_i^a$$

$$+ \sum_{i,a} \sum_j \langle ij || aj \rangle t_i^a + 1/2 \sum_{i,a} \sum_{j,b} \langle ij || ab \rangle t_i^a t_j^b$$

or

$$E = \sum_{\substack{i>j \\ a>b}} \langle ij||ab \rangle (t_{ij}^{ab} + t_i^a t_j^b) + \sum_{i,a} \langle i|f|a \rangle t_i^a, \quad (8)$$

where the usual Fock operator expression is introduced.

Eq. (8) provides the energy given the amplitudes for double excitations,  $t_{ij}^{ab}$ , and single excitations  $t_i^a$  determined by Eq. (6). The molecular integrals and amplitudes in Eq. (8) pertain to the molecular orbitals associated with the transformed hamiltonian,  $H$ . These orbitals are permitted to change to assume a more optimum form by exploiting the transformation in Eq. (3). Since the coupled cluster results are invariant to any unitary transformation that only mixes excited orbitals (i.e.,  $a, b, c, d, \text{etc.}$ ) or occupied orbitals (i.e.,  $i, j, k, l, \text{etc.}$ ) among themselves, the changes due to the transformation arise by mixing the occupied orbitals with the excited orbitals. The transformation matrix  $\{\kappa_{rs}\}$  can be determined from the Hausdorff expansion by imposing a stationary condition on the orbitals.

From Eq. (7) and Eq. (3), we have

$$E = \langle \phi_0 | e^{-\kappa} H e^{\kappa} | \psi_{CC} \rangle. \quad (9)$$

Invoking the Hausdorff expansion through terms second-order in  $\kappa$ ,

$$E = \langle \phi_0 | H | \psi_{CC} \rangle + \langle \phi_0 | [H, \kappa] | \psi_{CC} \rangle + 1/2 \langle \phi_0 | [[H, \kappa], \kappa] | \psi_{CC} \rangle. \quad (10)$$

The stationary condition is accomplished by varying  $E$  with respect to the operator  $\kappa$ . Hence,

$$\begin{aligned} \delta E = 0 = & \langle \phi_0 | [H, \delta \kappa] | \psi_{CC} \rangle + 1/2 \langle \phi_0 | [[H, \delta \kappa] \kappa] | \psi_{CC} \rangle \\ & + 1/2 \langle \phi_0 | [[H, \kappa] \delta \kappa] | \psi_{CC} \rangle \end{aligned} \quad (11)$$

Eq. (11) defines the matrix elements,  $\kappa_{rs}$ , in the operator  $\kappa$ , via

$$\begin{aligned} \frac{\partial E}{\partial \kappa_{rs}} = 0 = & \langle \phi_0 | [H, X_r^\dagger X_s - X_s^\dagger X_r] | \psi_{CC} \rangle \\ & + 1/2 \langle \phi_0 | [[H, X_r^\dagger X_s - X_s^\dagger X_r] \kappa] | \psi_{CC} \rangle \\ & + 1/2 \langle \phi_0 | [[H, \kappa] (X_r^\dagger X_s - X_s^\dagger X_r)] | \psi_{CC} \rangle \end{aligned} \quad (12)$$

Since  $\kappa$  appears linearly in Eq. (12), by working out the commutator expressions, an equation for the matrix elements  $\{\kappa_{rs}\}$  is obtained. With these quantities defined, the transformation matrix in Eq. (1),  $U = e^\kappa$ , is determined. Hence, Eq. (12) provides  $\kappa$  for stationary values of the energy (assuming the transition state form). This defines a new set of molecular orbitals,  $\phi_u = \sum \phi_v U_{vu}$ . All molecular integrals are transformed to this new set. Then the coupled-cluster equations, Eq. (6) can be solved again for the transformed orbitals. Successive repetition of this procedure should give a coupled-cluster solution with an improved molecular orbital basis set.

Since,

$$\psi_{CC} = e^T |\phi_0\rangle = 1 + T_1 + T_2 + 1/2 T_1^2 + 1/2 T_2^2 + T_3 + \dots |\phi_0\rangle \quad (13)$$

the transition state formula of Eq. (10) only permits  $T_1$  and  $T_2$  to occur linearly in the determination of  $\kappa$ , since the other terms would have vanishing matrix elements with  $|\phi_0\rangle$ . This seems like a reasonable approximation for most problems, but in pathological cases the quadratic and higher terms become increasingly important, and it is just such pathological cases, where the orbital optimization is most useful.

Alternatively, variational expressions of the form

$$E = \langle \psi_{CC} | e^{-\kappa} \text{He}^{\kappa} | \psi_{CC} \rangle / \langle \psi_{CC} | \psi_{CC} \rangle \quad (14)$$

can be employed to determine equations for the  $\{\kappa_{rs}\}$  matrix elements. This has the advantage that a rigorous upper-bound expression is , so the orbitals should be "better", and that higher powers of  $T$  operators would contribute to this determination. But it is still necessary to truncate the Hausdorff expansion. Hence, the method is at best quasivariational. Furthermore, it is not clear at just what levels appropriate for the truncation of  $T$  or  $\kappa$ . Additional problems pertain to  $T$  being a non-hermitian operator while  $\kappa$  has to be chosen to be hermitian to maintain the unitary transformation property, and that unlike the usual coupled-cluster equations, whose commutation using the normal  $T$ , i.e.,  $e^{-T} \text{He}^T |\phi_0\rangle$  terminates at four-fold commutations, a unitary  $T$  or  $\kappa$  operator requires an infinite commutator series.

We are currently investigating the relationships among the several different ways of imposing variational conditions on the orbital optimized coupled-cluster equations.

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APPENDIX A

ELECTRON CORRELATION IN LARGE MOLECULES  
WITH MANY-BODY METHODS

by

Rodney J. Bartlett  
and  
George D. Purvis, III

BATTELLE  
Columbus Laboratories  
505 King Avenue  
Columbus, Ohio 43201

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sponsored by the New York Academy of Sciences.

BATTELLE  
Columbus Laboratories  
505 King Avenue  
Columbus, Ohio 43201

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## ABSTRACT

A goal of quantum chemistry in biomedical sciences is to provide accurate calculations of molecular interaction among biochemical molecules, drugs, carcinogens, etc. In this effort, there is a natural progression from semi-empirical quantum chemistry, to ab initio self-consistent field theory, to methods that properly include electron-correlation. As ab initio theories continue to develop, many more problems of biomedical interest can be addressed by accurate correlated methods. The intent of this contribution is to discuss many-body approaches to the correlation problem, i. e., many-body perturbation theory (MBPT) and coupled-cluster methods (CCM). Unlike most configuration interaction (CI) methods, MBPT/CCM offers a number of important features in the extension to larger molecules. These include the proper dependence of the correlated calculation on the size of the molecule (i.e., size-extensivity). This has significant consequences for predictions of ground and excited-state properties. These features will be illustrated by applications to selected molecules. It will be demonstrated that MBPT/CCM offers a natural generalization of SCF theory that is formally suitable for applications to some of the molecules that occur in biomedical studies.

## I. INTRODUCTION

In the applications of quantum chemical methods to problems involving biochemical molecules and their interactions, there is a natural progression from empirical or semi-empirical models and methods to ab initio self-consistent field (SCF) approaches, and eventually, to ab initio approaches that properly include the effects of electron correlation. The purpose of this contribution is to discuss the many-body methods<sup>(1-15)</sup> (i.e., many-body perturbation theory<sup>(1-3)</sup> [MBPT] and coupled cluster methods<sup>(4-7)</sup> [CCM]) for including electron correlation. The emphasis is on the advantages that these methods offer over the more traditional configuration interaction (CI) approaches in large molecule applications.

Semi-empirical models and methods, which should be used synergistically with experiment, are most properly employed to investigate trends among a series of similar molecules. Such methods can be used for rather large molecules relatively inexpensively, and are thus finding wide use in biochemistry and particularly in drug design.<sup>(16-20)</sup> On the other hand, in principle ab initio methods can provide hard, quantitative results for molecular systems, which can be potentially used to complement various experimental methods by providing answers to classes of problems that are not as amenable to experiment. An example would be identifying the transition state and activation barrier in a reaction.

In practice, however, ab initio quantum chemistry suffers from severe limitations, that have only permitted highly accurate results to be obtained for comparatively small molecules. These limitations are basically of three types: (1) Number of degrees of freedom in molecular systems;

(2) limited size of basis set that can be used; and (3) required degree of accuracy of the ab initio approach.

In the first category, the problem essentially revolves around the Born-Oppenheimer (or fixed nuclei) approximation, since the calculation of the electronic structure and energy must be repeated for each choice of coordinates for the nuclei. Limitations (2) and (3) pertain to each of these calculations while limitation (1) refers to the number of times the calculations must be repeated. For example, mapping out a potential energy surface for even a four-atom system with  $3N-6=6$  degrees of freedom, and computing 10 points for each degree of freedom, would amount to a million calculations. In quantum biochemistry, fortunately, one is not often interested in a complete energy surface, but usually only a few crucial bond lengths and angles that need to be optimized, but this is still a formidable problem. The development of SCF<sup>(21-23)</sup> and correlated gradient methods<sup>(24-26)</sup> is a welcome addition to the quantum chemist's repertoire, but even these techniques are only applicable to a few degrees of freedom.

To take an example in quantum biochemistry, consider a solvated molecule where it is recognized that the solvation characteristics are partially responsible for the conformation of the molecule which can directly affect a highly specific interaction. The only feasible approach to such a problem at present is the determination of analytic model potentials of the Lennard-Jones, generalized Morse, and other types, with parameters determined empirically,<sup>(27)</sup> or perhaps from highly accurate quantum chemical calculations of the component pieces of the larger system.<sup>(28,29)</sup> Then, these potentials can be used to handle most of the dynamical movement of the molecule and solvent, allowing the more accurate quantum chemical methods

augmented by gradient techniques to focus on the most crucial active site interactions. The results of this procedure, however, are no better than the accuracy of the individual calculations which are subject to limitations (2) and (3).

In Figure 1 is shown a schematic drawing that illustrates the dependence of an ab initio quantum chemical prediction on basis set and calibre of method. Just improving the basis set or method is not enough, but rather a systematic improvement in both is required.

Considering the basis set problem first, and depending upon the property of interest, it is a matter of opinion at just how many basis functions are required to obtain good SCF results for molecules; but, certainly one would want at least a minimum basis set of one Slater orbital (or contracted Gaussian orbital, i.e., SZ - single zeta) for each electron and probably two (DZ, double zeta) or more (DZP, double zeta + polarization). The number of molecular integrals needed to do an SCF calculation rises formally as  $n^4$  where  $n$  is the number of basis functions although for sufficiently large molecules this dependence can be reduced to  $n^2$ . The largest SCF calculations which have been done employ no more than  $\sim 300$  functions. This imposes a limit of at most 300 electrons, or more realistically  $\sim 100$  to 150 electrons explicitly considered.

The problem is further compounded when electron correlation is included. Except for second-order perturbation theory which will be considered in more detail in Section IV, correlated methods have a dependence on the number of basis functions of  $\sim n^6$ . Again, it is possible to reduce this by maybe two-orders of magnitude for sufficiently large molecules, but it is

evident that even fewer problems can be studied at the correlated level than at the SCF level.<sup>(30,31)</sup>

There has yet to be a really good idea for eliminating the basis set problem in quantum chemistry. Completely numerical SCF calculations have only been accomplished for a few diatomic molecules,<sup>(32)</sup> and nothing of general utility has yet emerged. At the cost of using unrealistic potentials, the numerical procedures of the type used in MS-X<sub>α</sub> have had some success.<sup>(33)</sup> From the viewpoint of basis set quantum chemical computations the development of effective potentials for the chemically inert electrons in heavy atom molecules is very useful.<sup>(34-38)</sup> Also, Gaussian lobe functions<sup>(39)</sup> chosen to represent the bonds in a molecule rather than located on the various atomic centers have reduced the number of basis functions while simplifying the calculations of the integrals.<sup>(40)</sup> Various integral approximations<sup>(31)</sup> and other clever schemes can also aid in making the calculations more efficient, but the basis set problem remains a fundamental limitation.

The third limitation above, as illustrated in Figure 1, pertains to the degree of accuracy of method that is required for the property of interest, which is the main concern of this contribution. Generally, SCF theory is considered to be adequate ( $\pm 10\%$ ) for molecular conformations, equilibrium molecular structure, and first-order properties, i.e., properties obtained as an expectation value over the SCF density, such as the electrostatic potential or dipole moments. On the other hand, correlated methods are considered absolutely necessary to predict electronic and photoelectronic spectra, to study binding energies and other thermochemical quantities in

reactions where bond breaking is occurring; and, most second- and higher-order properties like polarizabilities, shielding constants, magnetic susceptibilities, etc. Since many questions in quantum biochemistry revolve around one or another of the properties that need an accurate treatment of electron correlation, it is important to consider the characteristics that a correlated method should have if it is to be applied to the large molecules that occur in quantum biochemistry.

A few desirable characteristics for such a correlated approach are that the method should be

- size-extensive: (i.e., should scale properly with the size of molecule)
- generally applicable to a wide class of problems; (i.e., avoid specific formulations or choices of configurations.)
- efficient and cost-effective (i.e., provide large correlations corrections inexpensively)
- applicable to open-shells and excited states;
- able to correctly separate a molecule into its fragments.

Another condition that one might expect is that the method be variational, giving an upper bound for the total energy. Lacking a coordinate lower bound, we believe this is an unnecessary restriction since the quantities of interest in quantum chemistry are invariably energy differences like binding energies, which possess no rigorous variational properties even if the individual calculations are variational. Furthermore, except for a full CI, and a few

other isolated cases (generalized valence bond, GVB<sup>(41)</sup>, e.g.) a variational requirement is not consistent with the size-extensive condition above, which is felt to be much more important to satisfy for large molecules.

At the present state-of-the-art in correlated theory, the first three conditions are easily accomplished with MBPT. Any approach based upon the linked-diagram theorem is size-extensive. A large class of problems can be studied with single reference MBPT/CCM calculations provided that RHF (of a UHF open-shell solution) is an adequate starting point. For the cost-effective property, it will be shown that second-order perturbation theory, which is the simplest MBPT approximation, typically accounts for ~90 percent of the correlation energy in a basis set and significantly improves the SCF predictions of dissociation energies and molecular geometries. Since this requires only marginally more effort than an SCF calculation, since it is size-extensive, and has rather general utility, it is a very attractive lowest-order approximation.

The fourth requirement can be handled with many-body approaches such as equation-of-motion techniques,<sup>(42-44)</sup> or with CI, and the fifth is currently most easily achieved using CI methods. In the last case, the MBPT/CCM theory exists for this problem, but has not yet been implemented in a general purpose program.<sup>(45-47)</sup> In many cases, a UHF reference function will permit correct separation, but the path toward the separated limit is not always accurate.<sup>(9)</sup>

In Section II, the size extensive property of MBPT/CCM will be discussed in some detail since this is an extremely important condition for potential applications of correlated methods to large molecules.

Section III will present a brief discussion of the ideas in many-body theory that are important for large molecules, while the final section will focus on some applications to benzene to demonstrate the nature of correlation effects due to higher excitations in this prototype system. In this section emphasis will also be placed on the accuracy of the simplest approximation, second-order perturbation theory, which typically provides a very large part of the electron correlation effect as an inexpensive by-product of the SCF calculation.

## II. SIZE-EXTENSIVITY IN MOLECULAR CALCULATIONS

Probably the best way to illustrate the importance of quantum mechanical methods that scale properly with the size of a molecule is to consider the model problem of a lattice of separated electron pair bonds, such as  $H_2$  molecules, since this serves as a first approximation to any large molecule. This problem has been worked out by several investigators,<sup>(48,49,11)</sup> but it is pertinent enough to the discussion that it is worth presenting a version here.

Assume the  $H_2$  molecules are sufficiently far apart or separated by barriers so that they can be considered to be noninteracting. For simplicity, we will further assume that the component set of molecular orbitals for each  $H_2$  molecule are natural orbitals so that single excitations in the  $H_2$  wavefunction need not be considered. Then the intermediately normalized wavefunction for each molecule  $i$ , may be written,

$$\phi^M(i) = \phi_0^M(i) + \chi^M(i) \quad (1)$$

where  $\phi_0^M(i)$  is the first natural determinant (close to the Hartree-Fock solution) and  $\chi^M(i)$  is a sum of doubly-excited determinants including their appropriate coefficients. The norm of the function in Eq. (1) is  $1 + S$ , where

$$S(i) = \langle \chi^M(i) | \chi^M(i) \rangle \quad , \quad (2)$$

$$\langle \phi_0^M(i) | \chi^M(i) \rangle = 0 \quad . \quad (3)$$

The wavefunction for the lattice is

$$\phi^L = \prod_{i=1}^N (\phi^M(i) + \chi^M(i)) \quad (4)$$

Antisymmetry is disregarded since the molecules are noninteracting.

With  $H^L = \sum H(i)$ , the energy of the lattice

$$E^L = \frac{\langle \phi^L | H^L | \phi^L \rangle}{\langle \phi^L | \phi^L \rangle} = N E_{H_2}^M \quad (5)$$

where  $E_{H_2}^M$  is the energy of the  $H_2$  molecule. With  $\beta = \langle \phi_0^M(i) | H(i) | \chi_i^M(i) \rangle$ , which is essentially the correlation energy of the molecule,

$$E_{H_2}^M = E_0^M + \beta \quad (6)$$

A method is said to be "size-extensive" if the total energy calculated by the method is appropriately linear in  $N$ , as in Eq. (5).

Notice that the product wavefunction in Eq. (5) includes quadratic and higher product terms like  $\chi^M(i)\chi^M(j)$ , which correspond to simultaneous double-excitations on different centers, but are quadruple and higher-excitations in a super-molecule CI description. Since these terms arise from disjoint double excitations, they are fundamentally simple, but the standard CI framework is not able to exploit this inherent simplicity. This causes an innate error in truncated CI that becomes most important for larger molecules.

To investigate this, we can consider a reference wavefunction for the lattice of the form

$$\psi_0^L = \prod_{i=1}^N \phi_0^M(i) \quad (7)$$

with energy

$$E_0^L = \sum_{i=1}^N E_0^M(i) = NE_0^M \quad (8)$$

Using this reference function, the double-excitation CI (D-CI) wavefunction for the lattice is constructed as

$$\begin{aligned} \psi_{D-CI}^L &= \psi_0^L + \sum_{k=1}^N c_k \psi^L(k) \\ &= \phi_0(1) \phi_0(2) \dots \phi_0(N) + \sum_{k=1}^N c_k \psi_0^L X^M(k) / \phi_0(k) \\ &= \psi_0^L + c \sum_{k=1}^N \psi^L(k) \end{aligned} \quad (9)$$

The weighting coefficient,  $c$ , is the same for each  $H_2$  molecule in a noninteracting lattice. Using the expressions,

$$\langle X^M(i) | X^M(j) \rangle = \delta_{ij} S \quad (10)$$

$$\langle X^M(i) | H^L | X^M(j) \rangle = \delta_{ij} [E_{H_2}^M S - B] ,$$

$$\Delta E = E^L - NE_0^M$$

it follows that

$$\langle \psi_0^L | H^L | \psi^L(k) \rangle = \beta \quad (11)$$

$$\langle \psi^L(k) | H^L | \psi^L(\ell) \rangle = \delta_{k\ell} [N S E_0^M + (S-1)\beta] \quad (12)$$

From these matrix elements, the D-CI secular equation becomes

$$\Delta E - N c \beta = 0 \quad (13a)$$

$$\{\beta - [S \Delta E + (S-1)\beta]\} c = 0 \quad (13b)$$

Solving Eq. (13) simultaneously for  $\Delta E$  and  $c$ ,

$$\Delta E_{D-CI} = \beta \left[ \frac{-(1-S) \pm \sqrt{(1-S)^2 + 4SN}}{2S} \right] = \underset{N \rightarrow \infty}{N^{eff} \beta + 3\sqrt{N/S}} \quad (14)$$

The positive sign is required since  $\Delta E < 0$  and  $\beta < 0$ . Since the correct  $\Delta E = N\beta$ , D-CI is not size-extensive.

With the aid of a value for  $S$  in Eqs. (2) and (14) it is possible to get some feel for the size of these effects. From a natural orbital study by Davidson and Jones<sup>(50)</sup> of the 50 term Kolos-Roothaan<sup>(51)</sup> wavefunction for  $H_2$  at  $R = 1.40$ ,  $S$  for  $H_2$  is 0.0181. Some representative values are shown in Table I, along with values for a lattice of He atoms for comparison ( $S_{He} = 0.0083$ ). It is apparent that the error in the correlation energy as determined by D-CI can be significant even for modest numbers of electrons. It is also apparent that the errors are greater for typical covalent bonds than inner-shell electron

pairs as in He atoms. In fact, we will find that Table I can provide a rather accurate estimate of the effects of higher excitations simply by counting the number of electrons in covalent bonds and inner-shell electron pairs.

Since the product terms  $x^M(i)x^M(j)$  correspond to quadruple excitations in a super-molecule CI, while triple products are hexuple excitations, etc., the size-extensive property of MBPT/CCM, that is a consequence of the linked-diagram theorem,<sup>(1,2)</sup> is essentially a result of a more proper treatment of quadruple and higher excitations than in CI. Hence, a statement that size-extensivity is important in correlated calculations, is equivalent to the statement that quadruple and higher-excitations are important. Since the number of configurations in CI are proportional to the number of basis functions raised to the level of excitation included, the number of quadruple excitations generated from 100 basis functions would require  $\sim(100)^4$  or  $10^8$  configurations. Hence, better computational methods for including effects of higher-excitations in correlated calculations are extremely important. Many-body methods tend to take the intelligent viewpoint that removing the erroneous terms (i.e., unlinked diagrams) in D-CI is preferable to including higher-excitations. In practice, this viewpoint leads to computationally more tractable equations that are closer to those in D-CI.<sup>(7)</sup>

Since the correct density is in error by the neglect of the product terms in the wavefunctions, further analysis discussed elsewhere,<sup>(49)</sup> demonstrates that the density matrix obtained from a truncated CI reduces to

just the density computed from the reference function. If the latter is an SCF function we have

$$\lim_{N \rightarrow \infty} \rho^{\text{TCI}} = \rho^{\text{SCF}} \quad (15)$$

Similarly, for an excitation energy, (49)

$$\lim_{N \rightarrow \infty} (E_f^{\text{TCI}} - E_i^{\text{TCI}}) = E_f^{\text{SCF}} - E_i^{\text{SCF}} \quad (16)$$

Hence, size-extensivity affects more than the total energy.

One additional consequence worth mentioning is that in a typical reaction,



the heat of the reaction,  $\Delta H_{\text{rxn}} = \Delta H_f(C) + \Delta H_f(D) - \Delta H_f(A) - \Delta H_f(B)$ .

However, if these individual quantities are determined by a truncated CI this simple addition is not entirely justified, since the truncated CI ignores the simultaneous excitations that prohibit  $\Delta H_f(C+D)$  at  $R_{CD} \rightarrow \infty$  from being  $\Delta H_f(C) + \Delta H_f(D)$ . In practice, this frequently requires that one compute the super-molecules  $C + D$  and  $A + B$  in CI to make the energy difference most accurate. This should be contrasted to predictions made with a size-extensive method where a table of results for species obtained at a given level of approximation may be added and subtracted just like the experimental values.

### III. SYNOPSIS OF MANY-BODY THEORY

The theory of MBPT/CCM has been discussed in detail in several places.<sup>(1-7)</sup> In particular reference [7] provides a fairly detailed mathematical description from the viewpoint taken in this article. The theory as originally developed, uses second-quantization and diagram techniques, which are unfamiliar to many-quantum chemists, and this tends to camouflage the important concepts that emerge from the many-body approach. Instead of presenting any detailed mathematical development here, we will sketch the basis for the two significant concepts that emerge from MBPT/CCM, namely the linked-diagram theorem, which guarantees size-extensivity, and the cluster decomposition of CI excitations into separate, more physically satisfying pieces that lead to tractable equations for including the effects of higher excitations. Consult reference [7] for detailed equations, and the original references<sup>(1-6)</sup> for the complete formal development. For simplicity, in the following we will limit ourselves to a single reference function such as an unrestricted Hartree-Fock (SCF) solution. Various versions of the multi-reference function theory are available.<sup>(45-47)</sup>

It is well-known that one way to solve a CI eigenvalue equation is with perturbation theory.<sup>(52)</sup> Using the Rayleigh-Schrodinger form, we can separate the hamiltonian  $H = H_0 + V$ , where  $H_0$  is the sum of the SCF one electron hamiltonians and  $V$  is the two-electron part minus the SCF effective one particle hamiltonian, then we have

$$H_0 \phi_0 = E_0 \phi_0$$

$$H_0 D_{ijk}^{abc} = E_{ijk}^{abc} D_{ijk}^{abc} \quad (18)$$

for  $\phi_0$  the SCF solution, and  $D_{ijk}^{abc}$  the various determinants that can be formed by replacing occupied SCF orbitals with excited SCF orbitals. The CI eigenvalue through fourth-order, then becomes

$$E = E_0 + \langle \phi_0 | V | \phi_0 \rangle + \langle \phi_0 | VR_0 V | \phi_0 \rangle + \langle \phi_0 | VR_0 (V - \langle V \rangle) R_0 V | \phi_0 \rangle \quad (19)$$

$$+ \langle \phi_0 | VR_0 (V - \langle V \rangle) R_0 (V - \langle V \rangle) R_0 V | \phi_0 \rangle - \langle \phi_0 | VR_0 V | \phi_0 \rangle \langle \phi_0 | VR_0^2 V | \phi_0 \rangle$$

The resolvent,  $R_0$ , has the expression

$$R_0 = |h\rangle \langle h| E_0 - H_0 |h\rangle^{-1} \langle h| \quad (20)$$

where  $|h\rangle$  is composed of all the CI excitation  $D_{ij}^{abc}$ . Even though  $|h\rangle$  is formally complete, Slater's rules for matrix elements chooses from all possibilities only the few that have nonvanishing contributions.

Subject to an SCF reference function, only double-excitations can mix across  $V$  with  $\phi_0$ , so the second- and third- order terms in Eq. (19) involve only double-excitations. The first of the two terms in fourth-order, however, can mix single, double, triple, and quadruple excitations at the middle  $R_0$ , although the second fourth-order term (i.e., the renormalization term) still has no contributions except from double excitations.

From the model problem of separated  $H_2$  molecules presented in the previous section, it is easy to check whether each of the terms in Eq. (19) is size-extensive. Considering the second-order energy of the  $H_2$  lattice

$$E_2^L = \langle \phi_0 | V R_0 V | \phi_0 \rangle \quad (21)$$

as an example, we have from Slater's rules

$$E_2^L = 1/4 \sum_{i,j}^{n_{occ}} \sum_{a,b}^{n_{exc}} |\langle ij || ab \rangle|^2 / (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b) \quad (22)$$

The notation  $\langle ij || ab \rangle = \langle ij | ab \rangle - \langle ij | ba \rangle = (ia | bj) - (ib | aj)$ , and  $\{\epsilon_i\}$  and  $\{\epsilon_a\}$  are the SCF orbital energies for the occupied and excited orbitals, respectively. Using a little algebra,

$$E_2^L = 2 \sum_{i < j} \sum_{a < b} [(ia | jb)^2 - (ia | jb)(ib | ja)] / (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b) \quad (23)$$

Since this expression is invariant to any unitary transformation among degenerate orbitals, we may choose the orbitals to be localized on the  $H_2$  molecules in the lattice to make the argument most transparent. In this case the only nonvanishing integrals have the charge distribution  $(ia)$ ,  $(jb)$ ,  $(ib)$  or  $(jc)$  on the same  $H_2$  molecule, otherwise the terms would vanish. Hence, it follows that

$$E_2^L = N E_2^M \quad (24)$$

and second-order perturbation theory is size-extensive. It can be similarly shown that this is also true for  $E_3$ .

Now consider fourth-order. The renormalization term is composed of an  $E_2$  term and a similar term  $\Delta = \langle \phi_0 | VR_0^2 V | \phi_0 \rangle$  which differs from  $E_2$  only by having the denominator squared. Since

$$E_2^L = NE_2^M, \quad \Delta^L = N\Delta^M, \quad (25)$$

The product of the two has an  $N^2$  dependence, which is erroneous. If  $E_4$  is to be size-extensive, the first term in  $E_4$ , must also have an equal and opposite  $N^2$  dependence to cancel out these uncharacteristic terms. The single-, double-, and triple-excitation contributions to the first part of  $E_4$  can be shown to be size-extensive. Hence, to resolve the problem, it is necessary to consider the quadruple excitation contributions. Following a great deal of algebra,<sup>(7)</sup> the quadruple excitation part,  $E_4^Q$ , may be written in the form,

$$E_4^Q = E_2\Delta + Q \quad (26)$$

where  $Q$  is properly size-extensive. Hence,  $E_2\Delta$  cancels the renormalization term and with it, the erroneous  $N^2$  dependence. This is the substance of the linked-diagram theorem. The algebraic analysis that leads to Eq. (26), represents  $Q$  as linked diagrams, while  $E_2\Delta$  corresponds to unlinked diagrams. A similar analysis will apply in all higher orders which is the linked-diagram theorem.<sup>(2)</sup> This provides the expression for the energy,

$$E = E_0 + \sum_{p=0}^{\infty} \langle \phi_0 | V[(E_0 - H_0)^{-1} V]^p | \phi_0 \rangle_L \quad (27)$$

where  $L$  limits the terms to only linked-diagrams.

It should be evident, that if quadruple excitations had not been included in  $E_4$ , then the  $E_2\Delta$  term with the erroneous  $N^2$  dependence would remain. This is exactly what happens when a truncated CI calculation is made. Limiting the configurations to single- and double-excitations, for example, will necessarily retain these erroneous terms destroying the size-extensivity of the method. If quadruple excitations were to be included in the CI, the result would be size-extensive through fifth-order, but would fail in six and higher-orders due to hextuple excitations. On the other hand, any approximation to the linked diagram theorem, Eq. (27), is size-extensive. This means that even second-order perturbation theory can be much better than very good CI calculations for sufficiently large molecules.

For small molecules, multi-reference CI techniques, that incorporate at least the most important quadruple excitations as double-excitations from a double-excitation reference space, will be size extensive for most practical purposes. GVB calculations are size-extensive, but GVB-CI will be only approximately size-extensive unless all excitations into the GVB orbitals are included. Since GVB provides a better choice of orbitals than SCF, and since one includes higher-level excitations than is normal in SCF based CI approaches, GVB-CI will usually be closer to size-extensive than other CI methods. An added advantage is that within the GVB method it is often possible to ensure correct separation.

The other important idea developed in many-body theory is the cluster expansion of the wavefunction. The basic concept is that the correct wavefunction may be written as  $e^T|\phi_0\rangle$ , where  $T$  is an operator. This form of the wavefunction ensures the linked-diagram, size-extensive basis of the theory.

Then  $T$  has the form

$$T = T_1 + T_2 + T_3 + \dots \quad (28)$$

where  $T_1, T_2, \dots$  are one-body, two-body, ... cluster operators. The  $T_2$  operator generates double-excitations with amplitudes to be determined by the coupled-cluster equations,<sup>(5-7)</sup> but the exponential form

$$e^T = T + 1/2 T^2 + 1/3! T^3 + \dots \quad (29)$$

causes some very different things to happen than in the CI approach. To see this, consider the CI operator for quadruple excitations,  $C_4$ . By equating the CI and coupled-cluster expressions for the quadruple excitations, we have

$$C_4 = T_4 + 1/2 T_2^2 + 1/4 T_1^4 + 1/2 T_1^2 T_2 + T_1 T_3 \quad (30)$$

Physically, what does this mean? Roughly,  $T_4$  represents an interaction among four electrons while  $T_2^2$  represents two simultaneous interactions of two electrons. A transformation to Brueckner orbitals makes  $T_1$  vanish, while  $T_1$  is usually small even for SCF orbitals so the final three terms are negligible most of the time. Since the normal electrostatic hamiltonian has no more than two-electron operators, simultaneous two-electron interactions would seem to be much more frequent in molecules, than "true" four electron interactions. From another viewpoint, the  $NH_2$  lattice problem emphasizes the neglect of simultaneous double-excitations on different  $H_2$  molecules, which is exactly what  $T_2^2$  offers. Thirdly, from perturbation theory, it may be shown that all the fourth-order quadruple excitation terms arise from  $T_2^2$ .<sup>(7)</sup>

with  $T_4$  only contributing in fifth- and higher-orders. Consequently, it was suggested by Sinanoglu<sup>(14)</sup> that  $C_4 = 1/2T_2^2$  is a very good approximation. Using this ansatz, we have the coupled-cluster doubles (CCD) approximation for the wavefunction,  $e^{T_2}|\phi_0\rangle$ . This leads to a set of nonlinear equations for the  $T_2$  amplitudes but there are only as many of these amplitudes as in a D-CI<sup>(5,7)</sup>. This provides the benefit that we have a size-extensive method; it is infinite-order although restricted to  $T_2$ , and we have no more amplitudes than in a D-CI calculation even though the effect of quadruple excitations are included. Since CCD reduces in fourth-order perturbation theory to double- and quadruple-excitation diagrams, it is straightforward to solve the CCD equations as successive iterations of a fourth-order MBPT calculation (7). Hence, couple-cluster methods may be viewed as complementary to MBPT when higher-order corrections are needed as can become important in pathological cases.<sup>(9)</sup>

#### IV. ILLUSTRATION OF MBPT/CCM RESULTS FOR SOME SMALL MOLECULES

The simplest approximation to the correlation energy in MBPT (assuming an SCF reference function for simplicity) is given by the second-order perturbation theory expression of Eq. (22).

Since the molecular orbitals  $i, j, \dots a, b, \dots$  and their orbital energies  $\epsilon_i, \epsilon_j, \dots \epsilon_a, \epsilon_b$ , are obtained from an SCF calculation, all the information is available that is needed for a correlated calculation except for a partial integral transformation, if used. The SCF calculation generates a set of two-electron integrals relative to atomic (i.e., primitive) basis functions, and in the general case an integral transformation is required to obtain the integrals relative to the molecular orbitals, i.e.,  $\langle ab || cd \rangle$ , which depends on the number of basis functions as  $n^5$ ; or, alternatively, a direct calculation of  $E_2, E_3$ , in terms of the integrals relative to atomic orbitals (probably orthogonalized) is required. In the case of  $E_2$ , however, only a very small number of integrals are required, since each integral involves only two occupied and two unoccupied orbitals. Consequently,  $E_2$  requires no more than  $n_{\text{occ}}^2 n_{\text{exc}}^2 \sim n^4$  operations, or less than in the SCF calculation itself. In a sufficiently large molecule where the primitive integrals  $\langle \alpha\beta || \gamma\delta \rangle$  vanish unless  $\alpha$  and  $\beta$  are in the same neighborhood as are  $\gamma$  and  $\delta$ , and unless the charge distributions  $\langle \alpha\beta \rangle$  and  $\langle \gamma\delta \rangle$  are not too far apart, the SCF calculations goes as  $n^2$ . In this case, evaluating  $E_2$  directly in terms of  $\langle \alpha\beta || \gamma\delta \rangle$  will permit a similar simplification, hence  $E_2$  can always be evaluated as a by-product of large SCF calculations at negligible additional expense.

This approximation is certainly recommended by convenience, but how reliable an approximation is it for the correlation energy? In Table II

are shown the fractions of the correlation energy within a basis set given by  $E_2$ ,  $E_3$ , and the fourth-order contributions just from double- and quadruple-excitations diagrams<sup>(7,9)</sup> for a variety of molecules. Using an SCF starting point,  $E_2$  and  $E_3$  are solely determined by double-excitations, with single-, double-, triple-, and quadruple-excitations appearing in fourth-order, but in the interest of also comparing the higher-order corrections obtained by the CCD (coupled-cluster doubles) approximation, which includes only double-excitations and the disjoint (i.e.,  $T_2^2$ ) quadruple-excitations to all orders, the single- and triple-excitations contributions are omitted from Table II.

It is apparent from the table that the simple second-order approximation accounts for the vast majority of the correlation energy obtainable within the basis set. A few generalizations about the results may be made. In multiply bonded systems such as  $N_2$ , CO, and  $CO_2$ ,  $E_2$  tends to slightly overestimate the net correlation energy in the basis set, while for saturated systems like  $H_2O$ ,  $CH_4$ , etc., it is more likely to underestimate the effect. HCN and benzene are intermediate. In a case where near degeneracy plays a role such as  $BH_3$ , convergence of the perturbation theory is much slower making  $E_2$  a poorer approximation. No particular differences are observed for open-shell molecules when UHF-SCF instead of an RHF-SCF solution is used as the unperturbed solution. On the average, it is clear that  $E_2$  accounts for ~90 percent of the correlation energy obtainable within the basis set. Since these basis sets are good enough that they account for ~70 percent of the "experimental" valence shell correlation energy,<sup>(9)</sup> this means  $E_2$  gives ~60 percent of the experimental valence correlation energy. It is also clear that DQ-MBPT(4) is usually very close to the infinite-order CCD model.<sup>(9)</sup> This is a common occurrence except for cases where near degeneracy is a problem.

In Table III are shown some thermochemical results obtained from  $E_2$  compared to higher-order correlation approximations. Although  $E_2$  predictions are not as good as the better approximations, they are clearly superior to the SCF predictions, again, providing most of the observed correlation corrections.

A similar result can be obtained for second-order predictions of molecular structure, where on the average ~50 percent of the error in the SCF geometries is removed.<sup>(11)</sup>

To obtain the exceptional accuracy reflected in Table III and reported elsewhere<sup>(53, 54)</sup> for various properties of small molecules, it is necessary to go beyond second-order, but for large molecules, the simplicity and comparatively high accuracy of this approximation demands that it be used to augment any large-scale SCF calculation of biochemical interactions.

Benzene serves as a prototype of many of the large, conjugated molecules that occur in biochemistry. As such, it is appropriate to analyze the higher order MBPT/CCM description of electron correlation in benzene to develop some feeling particularly for the effect of quadruple excitations.

The basis set is a standard Dunning double zeta contraction of Huuzinaga's 9s5p primitive Gaussian basis for carbon and the two H 1s orbitals corresponding to a Slater exponents of 1.2, giving 72 CGTO. The SCR energy of -230.6369 differs by 0.113 a.u. from the SCF results for a DZP basis and 0.18 a.u. from the estimated SCF limit.<sup>(58)</sup> The C(15<sup>2</sup>) electrons are kept frozen at the SCF level so the correlated calculations only pertain to the valence correlation energy. Polarization functions are usually found to be more important for correlation effects than in the SCF calculation itself, so the current DZ predictions should underestimate the magnitude of

the valence correlation energy. Even so, it is apparent from Table IV, that quadruple excitations amount to  $\sim 20$  percent of the predicted correlation energy.

In an attempt to study the origin of the quadruple excitation effects, the occupied and excited pi-orbitals were removed and the calculation repeated to give a value for just the sigma framework excited solely into unoccupied sigma orbitals. The same procedure was carried out for the pi-electrons. These results are reported in the second and third columns of Table IV.

The sigma framework accounts for over half of the net quadruple excitation effect, while the correlation effects of the delocalized pi-electrons are relatively independent of the quadruple excitations. Since the former involves 12 roughly independent covalent bonds, from Table I and Eq. (14), one would estimate an effect of  $\sim 14$  percent in reasonable agreement with the calculated 12 percent. The effect of the quadruple excitations on the pi-electron bonds is much smaller, but this is primarily due to the fact that only three bonds are possible. If the appropriate  $S$  for the pi-structure were as small as in He, the estimated effect of quadruple excitations would be 1.6 percent. The remaining correlation effects come from the sigma-pi interactions. It is interesting that excitation of sigma electrons into pi-excited orbitals and vice-versa results in  $\sim 13$  percent of the correction energy.

The DZ basis used here is capable of providing only about 49 percent of the experimental valence correlation energy.<sup>(58,59)</sup> Polarization functions would improve this result by about 20 percent.<sup>(9)</sup> Since the quadruple excitations are also responsible for more than 20 percent of the correlation energy, the

size of error encountered in SD-CI is as severe as excluding polarization functions from the basis set. Since the effect of quadruple and higher CI excitations will inevitably increase as larger molecules than benzene are studied, a correlation method that does not account for such effects has little hope of contributing to the investigation of biochemical interactions.

TABLE I. ERRORS IN D-CI AS A FUNCTION OF N FOR  
A LATTICE OF  $\text{NH}_2$  MOLECULES AND  $\text{NHe}$  ATOMS

N	$\text{H}_2$		He	
	$N^{\text{eff}}$	% Error in Correlation Energy	$N^{\text{eff}}$	% Error in Correlation Energy
2	1.97	1.5	1.98	0.8
4	3.81	4.8	3.91	2.4
6	5.54	7.7	5.77	3.8
8	7.19	10.1	7.58	5.2
10	8.77	12.3	9.35	6.5
20	15.8	21.1	17.6	12.1
50	32.0	35.6	38.2	23.6
100	51.0	48.0	65.2	34.8
1000	209.5	79.1	292.2	70.8

TABLE II. PERCENTAGE CONTRIBUTION OF DIFFERENT ORDERS OF PERTURBATION THEORY

<u>Molecule</u>	<u>Second-Order</u>	<u>Third-Order</u>	<u>Fourth-Order (DQ)</u>	<u>Higher Order (DQ)</u>
BH <sub>3</sub>	80.0	16.5	3.0	0.50
H <sub>2</sub> O	97.7	1.5	0.7	0.06
NH <sub>3</sub>	94.3	5.0	0.6	0.12
CH <sub>4</sub>	89.6	9.3	0.9	0.16
CO	100.0	-1.6	1.6	-0.09
CO <sub>2</sub>	103.2	-4.1	0.9	0.0
HCN	98.0	0.7	1.0	0.18
N <sub>2</sub>	101.0	-2.2	1.3	-0.11
C <sub>6</sub> H <sub>6</sub>	95.6	0.6	3.8	—
CH <sub>3</sub> CN	96.5	-2.2	3.7	—
B <sub>2</sub> H <sub>6</sub>	85.2	13.2	1.6	—

<sup>a</sup> In every example but C<sub>6</sub>H<sub>6</sub>, the basis set of at least of double zeta plus polarization quality. In C<sub>6</sub>H<sub>6</sub>, a double zeta basis is used.

TABLE III. COMPARISON OF THERMOCHEMISTRY RESULTS  
OBTAINED BY SCF AND MBPT WITH EXPERIMENT  
[All basis sets are at least DZP quality.]

Reaction	Method	-ΔE (kcal/mole)			Experiment
		SCF	E <sub>2</sub>	MBPT/CCD	
2 BH <sub>3</sub> → B <sub>2</sub> H <sub>6</sub> <sup>a</sup>	SDQ-MBPT(4)	18.5	37.5	35.6	36.6 ± 2 <sup>f</sup>
BH <sub>3</sub> + CO → H <sub>3</sub> BCO <sup>a</sup>	D-MBPT(4)	8.0	25.1	20.5	20.4 ± 2 <sup>f</sup>
BH <sub>3</sub> + NH <sub>3</sub> → H <sub>3</sub> BNH <sub>3</sub> <sup>a</sup>	D-MBPT(4)	20.5	32.0	30.1	--
HNC → HCN <sup>b</sup>	SDQ-MBPT(4)	10.7	18.0	15.0	(10.3 ± 1) <sup>g</sup>
HNC → [H <sub>N</sub> <sup>C</sup> ] <sup>b</sup>	SDQ-MBPT(4)	-33.4	-30.1	-29.5	--
BNC → BCN <sup>b</sup>	SDQ-MBPT(4)	-18.9	-9.8	-9.4	--
LiNC → LiCN <sup>b</sup>	SDQ-MBPT(4)	-6.4	-2.3	-3.8	--
CH <sub>3</sub> NC → CH <sub>3</sub> CN <sup>c</sup>	SDQ-MBPT(4)	19.2	26.2	22.8	23.7 ± 14 <sup>h</sup>
CH <sub>3</sub> NC → [CH <sub>3</sub> <sup>N</sup> <sub>C</sub> ] <sup>c</sup>	SDQ-MBPT(4)	-44	-40	-40	-38.4 <sup>i</sup>
H + CO → HCO <sup>d</sup>	CCD	4.8	11.8	13.6	15.7 ± 1.5 <sup>j</sup>
HCO → [HCO] <sup>d</sup>	CCD	-12.8	-17.4	-18.1	--
H <sub>2</sub> CO → H <sub>2</sub> + CO <sup>e</sup>	CCD	-7.2	-3.9	-3.9	-1.9 <sup>k</sup>
H <sub>2</sub> CO → H + HCO <sup>e</sup>	CCD	-68.6	-82.8	-86.0	86.0 ± 1.0 <sup>l</sup>

- <sup>a</sup> Reference [53].
- <sup>b</sup> Reference [55]. Square bracket indicates a transition state.  
This result includes a 4 kcal/mole zero point correction  
for the transition state.
- <sup>c</sup> Reference [54]. Square bracket indicates a transition state.  
This result includes a 4.8 kcal/mole zero point correlation.  
for the transition state.
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TABLE IV EFFECT OF QUADRUPLER EXCITATIONS ON THE CORRELATION ENERGY OF BENZENE

	All Valence Electrons	Sigma Electrons (only)	Pi Electrons (only)
$E_{SCF}$	-230.6369	--	
$E_2$	-0.4922	-0.3622	-0.0539
$E_3$	-0.0030	-0.0005	-0.0177
S	-0.0028	-0.0021	-0.0002
D	-0.0272	-0.0123	-0.0079
Q	+0.0079	+0.0074	+0.0012
$E_4(SDQ)$	-0.0229	-0.0070	-0.0069
SDQ-MBPT(4)	-0.5172	-0.3697	-0.0785
Experimental Valence Correction Energy	(-1.065)		
CCD	--	-0.3671	-0.0850
SD-RSPT(4) SD-CI	-0.4160	-0.3259	-0.0774
No effect of Quadrupole Excitations	-0.1012(20%)	-0.0438(12%)	0.0011(1%)

<sup>a</sup> All energies are in Hartree atomic units.

FIGURE 1. ILLUSTRATION OF THE DEPENDENCE OF AN AB INITIO CALCULATION ON THE BASIS SET AND ON THE QUALITY OF THE THEORY

SZ, SZP, DZ, AND DZP ARE RESPECTIVELY SINGLE ZETA, SINGLE ZETA PLUS POLARIZATION, DOUBLE ZETA, ETC. CONFIGURATION INTERACTION (CI) IS USUALLY ACCOMPLISHED BY ADDING SINGLE AND DOUBLE EXCITATIONS. MBPT AND CCM IN GENERAL EXCEED SD-CI IN ACCURACY SINCE EFFECTS OF HIGHER EXCITATIONS ARE INCLUDED TO SOME DEGREE. MR-CCSD INDICATES COUPLED-CLUSTER THEORY LIMITED TO  $eT_2 + T_2$  BUT RELATIVE TO MORE THAN ONE REFERENCE FUNCTION. THE BEST POSSIBLE SOLUTION IN A BASIS SET IS FULL CI.

## AB INITIO CALCULATIONS

[illegible]

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APPENDIX B

THE REDUCED LINEAR EQUATION METHOD IN COUPLED CLUSTER THEORY\*

by

George D. Purvis, III  
and  
Rodney J. Bartlett

BATTELLE  
Columbus Laboratories  
505 King Avenue  
Columbus, Ohio 43201

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# ABSTRACT

A numerical procedure for efficiently solving large systems of linear equations is presented. The approach, termed the reduced linear equation (RLE) method, is illustrated by solving the systems of linear equations that arise in linearized versions of coupled-cluster theory. The non-linear coupled-cluster equations are also treated with the RLE by assuming an approximate linearization of the non-linear terms. Very efficient convergence for linear systems and good convergence for non-linear equations is found for a number of examples that manifest some degeneracy. These include the Be atom,  $H_2$  at large separation, and the  $N_2$  molecule. The RLE method is compared to the conventional iterative procedure and to Padé approximants.

# I. INTRODUCTION

The basis idea of the coupled-cluster method (1-7) relative to a single reference function  $|\phi\rangle$ , is that the exact wavefunction may be written as  $\psi = \exp(T)|\phi\rangle$  where

$$T = T_1 + T_2 + \dots \quad (1)$$

and the excitation operators  $\{T_n\}$  are

$$T_n = 1/n! \sum t_{ijk\dots}^{abc\dots} x_a^+ x_b^+ x_c^+ \dots x_k x_j x_i \quad (2)$$

By back-projecting  $\psi$  onto  $\phi$  and a sufficient number of single, double, etc. excitations, non-linear algebraic equations of the form

$$a_i + \sum_j B_{ij} t_j + 1/2! \sum_{j,k} C_{ijk} t_j t_k + 1/3! \sum_{j,k,l} D_{ijkl} t_j t_k t_l \dots = 0 \quad (3)$$

occur. The quantities  $\{t_j\}$  are the amplitudes  $\{t_{ijk\dots}^{abc\dots}\}$  of Eq. (2) which are to be determined, while  $a_i$ ,  $B_{ij}$ ,  $C_{ijk}$ , etc., are simply combinations of molecular integrals. Unlike eigenvalue equations, the coupled-cluster equations are independent of the energy attesting to the linked-diagram, size-extensive nature of the theory.<sup>(7)</sup>

In most of the applications which have been made,<sup>(4-10)</sup> the trial function  $\psi_{\text{CCD}} = \exp(T_2)|\phi\rangle$  has been employed, which terminates Eq. (3) after quadratic terms,

$$\psi_{\text{CCD}} = (1 + T_2 + 1/2 T_2^2)|\phi\rangle \quad (4)$$

This model is referred to as coupled-cluster doubles (CCD),<sup>(7-9)</sup> or by Čížek as coupled-pair many-electron theory (CPMET).<sup>(3,4)</sup>

Another model called coupled-cluster singles and doubles CCSD can be defined by  $\Psi_{\text{CCSD}} = e^{T_1 + T_2} |\phi\rangle$ , which requires that  $T_1$  be included through the quartic terms while  $T_2$  still appears only quadratically. Since it is well-known that  $T_1$  can be completely eliminated by a transformation to Brueckner orbitals and that  $T_1$  is usually small for closed-shell (or UHF open-shell) SCF orbitals, the full CCSD model appears to be unnecessarily complex. Consequently, the simpler approximation which includes  $T_1$  only linearly, and which we will refer to as CCSD-1, is considered. (In Paldus, *et. al.*<sup>(5)</sup> this is referred to as approximation B). The trial function then becomes,

$$\Psi_{\text{CCSD-1}} = (1 + T_1 + T_2 + 1/2 T_2^2) |\phi\rangle \quad (5)$$

In Eqs. (4) and (5) a linearized version excluding the quadratic terms  $T_2^2$  has also been considered, both as a model and as a first approximation to the solution of the non-linear equations. In the case of CCD, this L-CCD model corresponds to the sum of all double-excitation diagrams to all orders, while L-CCSD includes the single excitation diagram as well. Both models are size-extensive as required by the linked-diagram theorem.<sup>(11,12)</sup> If the L-CCD or L-CCSD wavefunction were used in an expectation value formula to obtain the amplitudes, the non-size-extensive D-CI and SD-CI models would then emerge. In general, the quadratic term  $T_2^2$  results in a net positive contribution as explained elsewhere,<sup>(7)</sup> hence the L-CCD and L-CCSD models, though size-extensive, often provide correlation energies which are too low for the basis set. Since most of the other neglected terms like  $T_3$  also result in negative values, however, the net error is normally small, except for pathological cases usually involving near-degeneracies where the damping effect of the  $T_2^2$  term is quite important.<sup>(7,13)</sup>

Perhaps the most straightforward approach to the solution of Eq. (3) is to employ iterative techniques. Such successive iterations of Eq. (3) lead to various terms in the linked-diagram perturbation expansion, thereby providing a means to sum classes of MBPT diagrams to all orders.<sup>(3)</sup> This iterative method of solution makes it convenient to solve the coupled-cluster equations with the same techniques that are used to sum MBPT diagrams.<sup>(7,8)</sup> The rate of convergence can usually be significantly enhanced by employing Padé approximants,<sup>(14,16)</sup> which are simply resummations of the energies that come from successive iterations of the equations. However, there can be some difficulties with a straight-forward iterative approach.

For example, if the reference function used in the theory were comparatively poor it is unreasonable to anticipate that good convergence using a first-order method will occur. This has been demonstrated for  $N_2$ <sup>(17)</sup> and  $Be_2$ <sup>(7)</sup>, and will occur in almost any case where near degeneracies are a problem.<sup>(13)</sup> A common example in molecular theory is found when employing a restricted Hartree-Fock (RHF) solution as a reference function at large internuclear separations, where the RHF function erroneously separates to ionic products.  $H_2$  is a good example of this problem, since the  $1\sigma_u^2$  configuration becomes degenerate with the  $1\sigma_g^2$  RHF configuration at large separations. Also, Eq. (3) has many solutions,<sup>(18-20)</sup> so convergence to undesirable solutions is also possible. In some cases pertaining to excited states and excitation energies, it is necessary to obtain these other solutions to Eq. (3).<sup>(19,20)</sup>

An alternative method of solving Eq. (3) for the CCD case, has also been used.<sup>(5)</sup> This method neglects the quadratic term initially, solves the set of linear (L-CCD) equations exactly (perhaps by matrix inversion or

by iteration), and then uses a Newton-Raphson technique for the quadratic part.<sup>(5)</sup> A few repetitions of this procedure provides the solution. The main objection to this approach is that the linear terms tend to be negative while the non-linear contributions to the solution are positive. A simultaneous solution embracing both terms seems to be preferable to exploit the partial cancellation. In particular, an initial exact solution of the L-CCD equations tends to provide  $\{t_j\}$  that are often far away from the correct CCD  $\{t_j\}$ . In fact, the largest differences between CCD solutions and the L-CCD solutions occur for pathological cases,<sup>(7,13,17)</sup> which is exactly where improved methods of solution are required.

In an attempt to improve the convergence of the solution to the coupled cluster equations, we have investigated a technique originally proposed for configuration interaction (CI) eigenvalue equations termed the reduced partitioning (RP) procedure.<sup>(21-24)</sup>

In the CI case, the basic idea of this reduced partitioning technique is to drastically reduce the effective dimension of a CI eigenvalue problem, which is typically very large, by making a rectangular transformation of the CI hamiltonian matrix to a set of  $m$  trial functions (where  $m$  is small). The similarity with moment theory,<sup>(25)</sup> the Lanczos algorithm,<sup>(26)</sup> and Davidson's method for eigenvalue problems<sup>(27)</sup> is evident. In the following sections we show that it is also possible to use a reduce partitioning approach for linear equations. We also show that this reduced linear equation method can be used to improve convergence for the non-linear equations of the type that occur in coupled cluster theory.

In the following, this technique is described and illustrated by application to a few simple cases.

## II. THE REDUCED LINEAR EQUATION METHOD

The linear approximation to the coupled cluster equation (3) can be written in matrix form as

$$\underline{a} + \underline{B}\underline{t} = 0 \quad (6)$$

where  $\underline{a}$  and  $\underline{t}$  are column vectors and  $B$  is a diagonally dominant square matrix. In the L-CCD model,  $\underline{t}$  will be a vector with a length equal to the number of double excitations. For a closed shell molecule with  $n$  electrons and  $N$  basis functions, roughly  $n^2 N^2$  excitations are possible. Even if a molecule has twenty electrons and one hundred basis functions, vectors the length of  $\underline{t}$  can be conveniently managed on most medium-sized computers.

On the other hand,  $\underline{B}$  is a square matrix and the number of elements which must be processed depends upon the square of the length of  $\underline{t}$ . In the L-CCD model, we would have to consider up to  $n^4 N^4$  elements in  $\underline{B}$  - despite the fact that most of the elements are zero. For the model problem of twenty electrons and a hundred basis functions, the construction, storage and manipulation of  $\underline{B}$  as a matrix becomes impractical.

Fortunately,  $\underline{B}$  is constructed from a matrix containing only  $N^4$  elements, i.e., the molecular integrals, and efficient programs have been written which construct the products, like  $\underline{B}\underline{t}$  directly from the  $N^4$  elements. This is implicit in most many-body approaches and has also been exploited in direct CI techniques.<sup>(28,29)</sup> Thus, the  $n^4 N^4$  bottleneck is broken by never constructing  $\underline{B}$ . Instead, a program taking as input a trial vector  $\underline{t}^{(m)}$  and the  $N^4$  integrals directly yields a new quantity  $\underline{t}^{(m+1)}$ , which is used to find the solution  $\underline{t}$ . Since  $\underline{B}$  is not available, most standard methods for solving systems of linear equations are not applicable.

One simple iterative scheme can be derived by partitioning  $\mathcal{H}$  into a diagonal matrix  $\mathcal{D}$  and a non-diagonal matrix  $\mathcal{A}$ . Since  $\mathcal{D}$  has only the same number of elements as  $\mathcal{t}$ ,  $\mathcal{D}$  can also be managed on a computer. With this partitioning, Eq. (2) can be rewritten as

$$\mathcal{D}\mathcal{t} = -\mathcal{a} - \mathcal{A}\mathcal{t} \quad (7)$$

$$\mathcal{t} = -\mathcal{D}^{-1} (\mathcal{a} + \mathcal{A}\mathcal{t}) \quad (8)$$

Eq. (4) is easily changed into a first-order iterative equation

$$\mathcal{t}^{(m+1)} = -\mathcal{D}^{-1} (\mathcal{a} + \mathcal{A}\mathcal{t}^{(m)}) \quad (9)$$

where  $\mathcal{t}^{(m)}$  is the  $m^{\text{th}}$  iteration of Eq. (5) and where usually  $\mathcal{t}^{(0)} = 0$ .

If all the diagonal terms in  $\mathcal{H}$  are placed into  $\mathcal{D}$  so that the diagonal of  $\mathcal{A}$  is zero, then Eq. (5) is the Jacobi method for solving linear equations.<sup>(30)</sup> Under these conditions, Eq. (9) is the same as the perturbation equation for the L-CCD model assuming an Epstein-Nesbet partitioning of the Hamiltonian.<sup>(31)</sup>

In the past, the Møller-Plesset partitioning<sup>(32)</sup> has been demonstrated to be the best choice for solving perturbation or cluster equations.<sup>(16)</sup> The Møller-Plesset partitioning places the diagonal effective one-body terms (e.g., orbital energies) into  $\mathcal{D}$  and leaves the two-body terms in  $\mathcal{A}$ . The resulting iterative method is similar to the Jacobi method with over relaxation, however, here there is a different relaxation parameter associated with each diagonal element.

The slow convergence of the Jacobi method and related methods is well-known. To obtain more rapid coverage for the iterative solution of the

coupled cluster equations, we have adapted the reduced partitioning (RP) method previously applied to the eigenvalue problem.<sup>(21-24)</sup> In the RP method, the approximations obtained at each iteration are saved and then used on subsequent iterations to provide a subspace onto which Eq. (6) is projected and in which the projected system of equations is solved. For example, if  $m$   $t^{(i)}$ 's are available, then we set up a system of  $m-1$  equations

$$R_{ij} \tau = \alpha \quad (10)$$

where

$$\begin{aligned} R_{ij} &= \sum_{kl} t_k^{(i)} B_{kl} t_l^{(j)} \\ &= \sum_{kl} t_k^{(i)} (D_{kl} + A_{kl}) t_l^{(j)} \\ &= \sum_k t_k^{(i)} D_{kk} t_k^{(j)} - \sum_k t_k^{(i)} D_{kk} t_k^{(j+1)} - \sum_k t_k^{(i)} a_k \end{aligned} \quad (11)$$

and where

$$\alpha_i = \sum_k t_k^{(i)} a_k \quad (12)$$

Once  $\tau$  is determined, the best approximation to  $\tau$  using  $m$   $t^{(i)}$ 's is

$$t^{[m]} = \sum_{i=1, m-1} \tau_i t^{(i)} \quad (13)$$

The superscript  $[m]$  on  $t$  indicates that  $\tau$  has been obtained from  $m$   $t^{(i)}$ 's.  $t^{[m]}$  will be the same length as  $t$ . As can be seen from Eq. (8) and (9), the matrix elements for  $R$  and  $\alpha$  are easy to evaluate since they are only weighted overlap integrals between trial solutions of different iterations, giving Eq. (10). This small matrix problem

can then be solved with standard algorithms specifically designed for approximately singular matrices. It is important to note that the  $\tilde{R}$  matrix rapidly tends to singularity. However, when  $\tilde{R}$  is singular then  $t^{[m]}$  has probably remained unchanged for at least one iteration and we already have a solution.

Notice that it is optional whether the vectors  $t_k^{(i)}$  are not solutions or whether increments (i.e., successively higher orders "perturbation" corrections to the vector) are used, since the two approaches are related by a linear transformation. The latter approach is the choice in the RP eigenvalue problem<sup>(21,22)</sup> since the matrix elements in Eq. (10) could be conveniently related to perturbation energies and overlaps of perturbed wavefunctions.

In the following examples, the Jacobi type iteration scheme (c.f., Eq. (9)) has been used to generate the basis  $\{t_k^{(i)}\}$  in which the reduced linear Eq. (10) is solved. The  $\{t_k^{[n]}\}$  could provide an alternative basis; however, the convergence properties for the L-CCD and L-CCSD models would remain unaltered and a time consuming step-the construction of  $\{t_k^{[n]}\}$  would have been added.

Thus far we have described methods for solving linear equations. The general coupled-cluster equations are non-linear and it is of interest to ask whether the reduced linear equation method can be used for solving a matrix equation of the form of Eq. (3). As a simple first step, the quadratic term in Eq. (3) is written as an effective linear term

$$\gamma(t)_{ij} = \sum_k G_{ijk} t_k \quad (14)$$

so that a general pseudo-linear version of Eq. (3) limited to quadratic terms can be written as

$$a + B(t) t = 0 \quad (15)$$

where  $\mathcal{B}(\underline{t})$  is  $\mathcal{B} + \chi(\underline{t})$ . If we partition  $\mathcal{B}(\underline{t})$  into a diagonal matrix  $\mathcal{D}$  which does not depend upon  $\underline{t}$  and a non-diagonal matrix  $\mathcal{A}(\underline{t})$  which does depend upon  $\underline{t}$ , then equations (9), (11), (12), and (13) can still be used providing  $\mathcal{A}(\underline{t}^{(m)})$  is used whenever  $\mathcal{A}$  is specified. If the sequence

$$(\underline{t}^{(1)}, \underline{t}^{(2)}, \dots, \underline{t}^{(m)}, \dots) \quad (16)$$

converges, then the sequence of solutions

$$(\underline{\tau}^{[1]}, \underline{\tau}^{[2]}, \dots, \underline{\tau}^{[M]}) \quad (17)$$

to the reduced linear equations

$$\mathcal{R}^{(m)}(\underline{t}) \underline{\tau}^{[m]} = \mathcal{R}^{(m)} \quad m = 1, 2, 3, \dots, M \quad (18)$$

will converge to the same  $\underline{t}$  as the sequence in Eq. (14). If the iterative solution to Eq. (9) diverges, then the sequence of solutions to the reduced linear equations does not necessarily converge since  $\mathcal{B}(\underline{t})$  and  $\mathcal{R}(\underline{t})$  do not converge. Consequently, for the non-linear equations, it is useful to take the best available solution (i.e.,  $\underline{t}^{[m]}$ ) and use it to define  $\mathcal{B}(\underline{t}^{[m]})$ . Thus, a suggested process for non-linear equations is

$$\underline{t}^{(m+1)} = -\mathcal{D}^{-1}[\mathcal{A} + \mathcal{A}(\underline{t}^{[m]}) \underline{t}^{(m)}] \quad (19)$$

Alternative schemes for handling the problems of non-linearity in a linear framework may be envisioned. Such schemes must address questions concerning consistency of the final solution and the rate of convergence. In the following, we will apply the simple linearization method of Eqs. (14) and (15) to several linear and non-linear coupled cluster examples to illustrate the relative speed of convergence using the reduced linear equation (RLE) approach and for the simple linearization discussed above for the non-linear equations.

### III. DISCUSSION OF RESULTS

As a first example of the RLE technique consider the Be atom. In Table I are shown results for the two linearized coupled-cluster models, L-CCD and L-CCSD and the non-linear CCSD-1 model. The GCTO 7s3p basis is the same that has been used previously<sup>(33,7)</sup> and is within  $9 \times 10^{-5} h$  of the SCF limit. Since in Be, the 2s and 2p orbitals are close in energy, the  $1s^2 2p^2$  configuration is expected to be relatively important compared to the  $1s^2 2s^2$  reference configuration in the correlated wavefunction. In the intermediately normalized wavefunction, the correlating  $1s^2 2p^2$  configurations have coefficients of 0.14 for CCSD-1 and 0.16 for L-CCSD while other double-excitation configurations involving this 2p orbital have coefficients about half as large. The remaining coefficients are  $< 0.05$ . This might be compared with a problem like  $H_2O$  at equilibrium where the largest coefficient of any configuration is 0.049.<sup>(8)</sup> This feature manifests itself in comparatively slow convergence of perturbation theory for Be, as seen in Table I. On the other hand, the Padé approximant resummation is far more effective, and the reduced linear equation approach for the linearized models exceeds the convergence of the Padé approximants.

The first cycle of perturbation theory is the second-order Møller-Plesset energy<sup>(32)</sup> while at least the third-order perturbation result needs to be computed before either the [1,0] Padé approximant [i.e.,  $E_2/(1-E_3/E_2)$ , the geometric approximation] or the first cycle of the RLE is possible. In fact, for the linear theories it is possible to get two perturbation energies per iteration, using a version of the  $2n+1$  rule of perturbation theory.<sup>(16)</sup> This is not in general applicable to the non-linear coupled-cluster iterations, however.

The similarity between  $E_2 + E_3$ , obtained from the second-cycle of perturbation theory, and the  $[1,0]$  approximant attests to the relative smallness in this example of  $E_3^2/E_2$  and the other higher-order differences that distinguish the  $[1,0]$  approximant from  $E_2 + E_3$ . Analogously, the Padé approximants and the RLE results are also closely related, differing primarily in that an exact matrix problem is solved in the RLE case, while the Padé approximants offer an increasingly good approximation to the matrix equation solution.<sup>(15)</sup>

For the non-linear CCSD-1 equations, again the Padé analysis and the RLE analysis; assuming the simple linearization of Eq. (14) are vastly superior to the order-by-order iterative solution. However, the first-order iterative convergence for CCSD-1 is superior to that observed in the linearized models. This is because the incorporation of the quadratic, and positive,  $T_2^2$  term, into the iterative cycle enhances the speed of convergence, since  $T_2^2$  acts as a damping factor on the negative linear terms. In practice, two iterations of the linearized equation are made, followed by the first non-linear iteration. All subsequent cycles embrace a linear and non-linear iteration.

The main advantage of the Padé approximant analysis compared to the RLE, is that the Padé approximants are obtained solely from the energies computed at each iteration.<sup>(16)</sup> Once the energy is calculated, previous  $t_v$  vectors can be discarded. In the RLE, the matrix in Eq. (10) needs to be computed, and this requires overlaps among the different iterative cycles, which requires that these quantities be retained on mass storage. The Padé approximant analysis also has its disadvantages, however, in that they do not provide wavefunction information conveniently. In the RLE, the solution of the matrix problem gives a highly accurate representation of the wavefunction along with

the energy. In cases where  $\tilde{\epsilon}$  has not yet converged the RLE solution is available and exactly corresponds to the RLE energy. The RLE solution is also compact in the sense that it consists of just a few coefficients for the different  $\tilde{t}$  vectors. This can sometimes have advantages when using the wavefunction in different contexts, such as the prediction of second-order properties.<sup>(24)</sup>

Another difficult example for convergence of the coupled-cluster equations is offered by  $H_2$  at large separation. In this case, the reference  $1\sigma_g^2$  configuration becomes degenerate with the correlating double excitation,  $1\sigma_u^2$ . Any attempt to determine such a potential curve with only a single RHF reference function and finite order perturbation theory will become suspect at sufficiently large internuclear separation.

This is illustrated very clearly in Tables II and III, where results for  $R = 1.2$  and  $R = 6.0$  a.u. are compared. The L-CCD results converge reasonably well in the first case ( $\sim 1\mu h$ ), but remain 0.4 hartrees in error through the same cycle at 6 a.u. This behavior is also reflected in the coefficient of the  $1\sigma_u^2$  configuration which is 0.06 at 1.2 a.u. and 0.9 at 6.0 a.u. It is also evident that the L-CCD result is much too low at 6.0 a.u. compared to the CCD and CCSD-1 values, and in fact, will tend to minus infinity at large  $R$  due to singularities in the energy denominator. On the other hand, the L-CCD result is not very different than the CCD or CCSD-1 values at 1.2 a.u. For a problem with the degeneracy illustrated here, it is extremely important to retain the quadratic  $T_2^2$  terms to provide a reliable answer.<sup>(7)</sup>

As is found for Be, the non-linear CCD and CCSD-1 models show markedly better convergence than the L-CCD model. Whereas at 1.2 a.u. the improvement is

comparatively slight, at 6.0 a.u., there is a dramatic difference. In fact, the first-order iterative CCD solution converges as fast as the RLE or Padé approximants. The CCSD-1 has somewhat poorer convergence probably due to the failure to include  $T_1^2$  and  $T_1T_2$  into the model.

Figure 1 compares the size of the increments between successive cycles for the different models, the first-order iterative approach, the  $[N,N-1]$  and  $[N,N]$  Padé approximants, and the RLE results for the L-CCD and CCD solutions for  $H_2$  at  $R=6.0$  a.u. Rather than showing the convergence to a final result, this figure perhaps offers some idea of the stability offered by the different methods used to converge the solutions. The solid points refer to the non-linear CCD results, utilizing the simple linearization techniques of Eq. (14).

It is clear that the most stable results even for this highly degenerate problem are offered by the RLE solution to the L-CCD equations. The Padé approximants are very good, but they still tend to fluctuate at the  $\pm 10^{-8}$  level. The standard iterative, perturbation procedure retains large increments at about the  $10^{-1}$  level in all cycles shown.

For the non-linear CCD equations, there is little difference between the RLE, Padé, and straightforward iterative techniques. None of the approaches offer as much numerical stability as the RLE does for the linear problem. Rather the RLE and the Padé approximants tend to reduce the increment to  $\sim 10^{-9}$  in the 8-10 cycles, while even the iterative procedure goes down to  $< 10^{-8}$ . Again it is very clear that the iterative approach is vastly superior for CCD compared to L-CCD for this pathological example. Strictly speaking, the  $[N,N-1]$  and  $[N,N]$  Padé approximants correspond to two separate sequences, and their increments should be compared in that manner, but for this example there is no appreciable difference.

Very accurate convergence of the CCD solution has been found to be necessary to obtain the highly sensitive quartic force field that we have reported for the  $\text{H}_2\text{O}$  molecule.<sup>(8)</sup> In this example, convergence to less than  $10^{-10}$  could be readily detected in the force field determination.

In a final example, in Table IV, results for the CCD and CCSD-1 models for  $\text{N}_2$  are presented. At  $R=3.0$  a.u., the bifurcation into separate RHF and UHF solutions for  $\text{N}_2$  has already occurred,<sup>(17)</sup> causing a decided lack of stability in the RHF based coupled-cluster models. For example, some of the double excitation coefficients are already as large as 0.22, with several others lying in the range 0.11 to 0.06.

Except for the much larger number of electrons and the earlier onset of the instability,  $\text{N}_2$  behaves very much like  $\text{H}_2$ , in that an L-CCD solution, even at 3.0 a.u. will be much too negative and highly slowly convergent, while the CCD and CCSD-1 provide more realistic results. Again, the Padé approximants and RLE give relatively good convergence to the solution, both better than the iterative technique. The larger number of electrons does not seem to require that more cycles be run to get the solution, even though it is clear that the iterative technique is poorer for  $\text{N}_2$  than in  $\text{H}_2$ .

In conclusion, the reduced linear equation approach has been shown to be very efficient, accurate, and convenient for obtaining solutions of linear coupled cluster equations. This may have importance for solving a wider variety of linear equation systems. The RLE coupled with a simple, approximate linearization of the non-linear equations, is somewhat less satisfactory, but still at least as good as other techniques, and much better than a straightforward iterative approach. More sophisticated ways of

incorporating the non-linearity of the general coupled cluster equations that still give a quasi-linear system may be found that would allow the RLE approach to function more efficiently. The main advantage of the RLE procedure compared to a Padé approximant analysis, is the ease of obtaining the coupled-cluster wavefunction in addition to the energy.

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Figure 1. Increments between successive cycles in the convergence of the L-CCD and CCD equations for  $H_2$  at  $R = 6.0$  a.u. Solid points refer to the L-CCD equations and open points to the CCD equations.

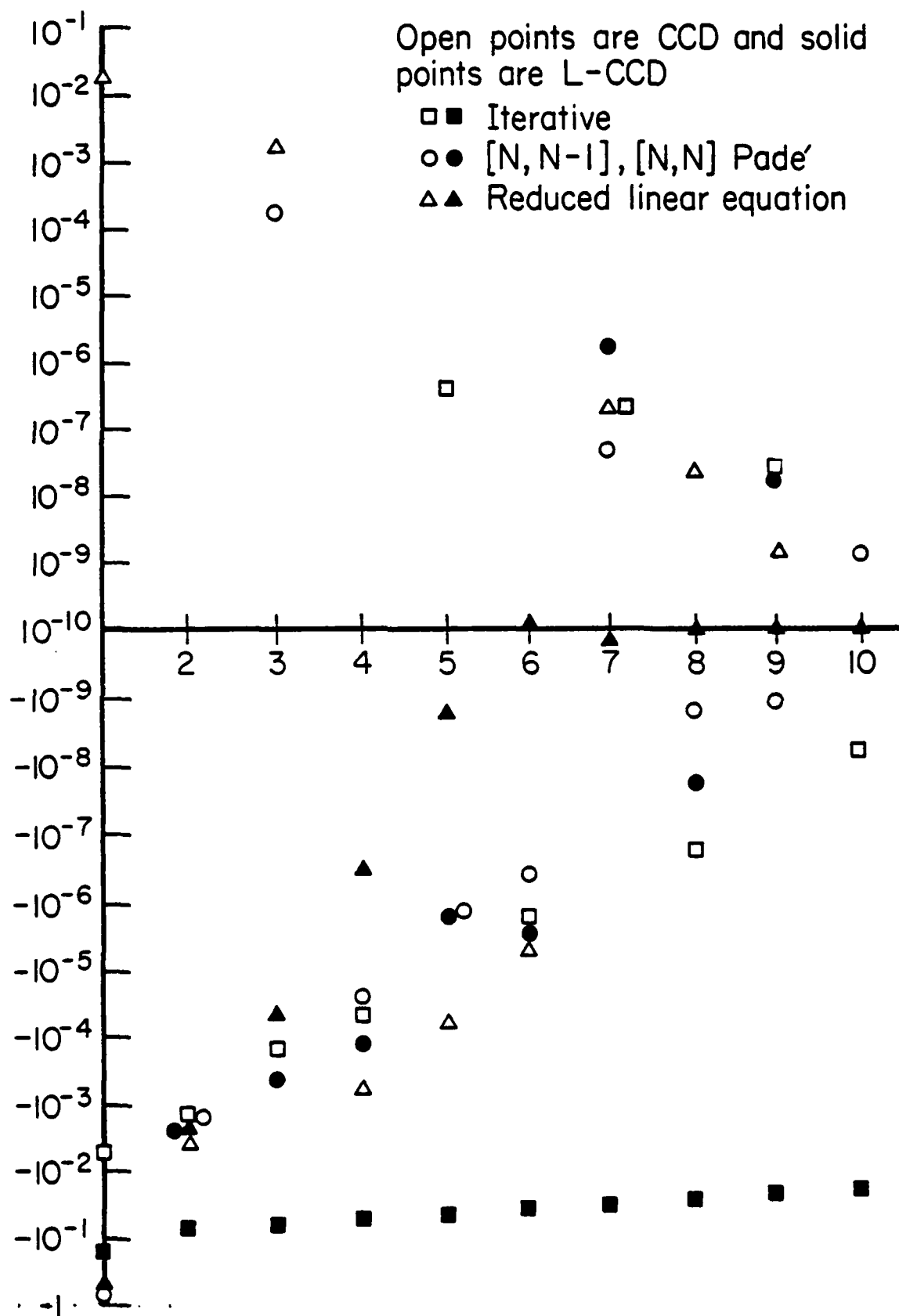


TABLE 1. CONVERGENCE OF L-CCD, L-CCSD, AND CCSD-1 MODELS FOR Be, (7s3p) CGTO BASIS.  
All energies are in hartree a.u.

Cycle Number	L-CCD			L-CCSD			CCSD-1		
	Perturbation Theory	[N,N-1],[N,N] Padé Approximants	Reduced Linear Equation	Perturbation Theory	[N,N-1],[N,N] Padé Approximants	Reduced Linear Equation	Perturbation Theory	[N,N-1],[N,N] Padé Approximants	Reduced Linear Equation
1	-14.626254	-14.631456	-14.630455	-14.626254	-14.631425	-14.630455	-14.625421	-14.629713	-14.629032
2	.631423	.638264	.638931	.631578	.639007	.639668	.629712	.634218	.634535
3	.634368	.639068	.639340	.634679	.639884	.640175	.631910	.634630	.634780
4	.636178	.639332	.63936005	.636623	.640170	.64019405	.633126	.634729	.634740
5	.637320	.639352	.63936091	.637871	.640188	.64019487	.633814	.634734	.634733
6	.638049	.639360	.63936096	.638679	.64019404	.64019490	.634207	.63473605	.63473589
7	.638516	.63936078		.639205	.64019478		.634432	.63473629	.63473659
8	.638810	.63936091		.639548	.64019487		.634561	.63473633	.63473640
9	.639010	.63936097		.639772	.64019491		.634636	.63473635	
10	.639134	.63936096		.639919	.64019490		.634678		
11	.639215			.640014			.634703		
12	.639266			.640077			.634717		
13	.639300			.640118			.634725		
14	.639322			.640144			.634730		
15	.639335			.640162			.634733		
16	.639345			.640173			.634734		
17	.639350			.640181			.634735		
18	.639354			.640186			.63473564		
19	.639357			.640189			.63473694		
20	.639358			.640191			.63473611		
-	.63936096			.64019490			.63473635		

TABLE 2. L-CCD, CCD, CCSD-1 CONVERGENCE FOR H<sub>2</sub> DZP (2s1p) CGTO BASIS. R = 1.2 a.u.  
Energies in hartree a.u.

Cycle Number	L-CCD			CCD			CCSD-1		
	Perturbation Theory	[N,il-1],[N,N] Pade Approximants	Reduced Linear Equation Method	Perturbation Theory	[N,N-1],[N,N] Pade Approximants	Reduced Linear Equation Method	Perturbation Theory	[N,N-1],[N,N] Pade Approximants	Reduced Linear Equation Method
1	-1.148990	-1.155837	-1.155853	-1.154244	-1.155498	-1.155541	-1.154244	-1.155557	-1.155541
2	-1.154443	-1.156420	-1.156443	-1.155497	-1.155980	-1.155982	-1.155556	-1.156090	-1.156095
3	-1.155835	-1.156444	-1.156452	-1.155845	-1.156000	-1.156008	-1.155936	-1.156111	-1.156120
4	-1.156247	-1.156451		-1.155952	-1.156004	-1.156004	-1.156056	-1.156117	-1.156118
5	-1.156380	-1.156452		-1.155986			-1.156096	-1.156118	
6	-1.156426			-1.156000			-1.156110		
7	-1.156442			-1.156002			-1.156115		
8	-1.156448			-1.156003			-1.156117		
9	-1.156450			-1.156004			-1.156117		
10	-1.156451			-1.156004			-1.156118		
-	-1.156452			-1.156004			-1.156118		

TABLE 3. L-CCD, CCD, CCSD-1 CONVERGENCE for  $H_2$  (2s1p) CGTO BASIS.  $R = 6.0$  a.u.  
Energies in hartree a.u.

Cycle Number	L-CCD			CCD			CCSD-1		
	Perturbation Theory	[N,H-1],[N,N] Padé Approximants	Reduced Linear Equation Method	Perturbation Theory	[N,N-1],[N,N] Padé Approximants	Reduced Linear Equation Method	Perturbation Theory	[N,N-1],[N,N] Padé Approximants	Reduced Linear Equation Method
1	-1.019757	-1.112977	-1.246073	-0.978141	-0.985878	-1.011540	-0.978141	-0.993395	-1.015540
2	-1.105169	-1.968948	-1.969843	-0.985818	-0.987746	-0.983820	-0.993161	-0.996344	-0.998739
3	-1.182896	-1.973987	-1.974048	-0.987359	-0.987512	-0.989051	-0.995787	-0.998309	-0.993571
4	-1.253665	-1.974105	-1.974109	-0.987498	-0.987556	-0.986739	-0.997049	-0.997419	-0.999377
5	-1.318102	-1.974107	1.974110	-0.987556	-0.987558	-0.987484	-0.997281	-0.997510	-0.997193
6	-1.376775	-1.974112		-0.987556	-0.987559	-0.987553	-0.997470	-0.997540	-0.997492
7	-1.430201	-1.974110		-0.987559			-0.997498	-0.997540	-0.997539
8	-1.478848			-0.987559			-0.997530	-0.987541	-0.997540
9	-1.523144			-0.987559			-0.997534		-0.997540
10	-1.563479			-0.987559			-0.997539		-0.997541
-	-1.974110			-0.987559			-0.997541		

TABLE 4. CCD AND CCSD-1 CONVERGENCE FOR  $N_2$  (4s3p1d) CGTO BASIS.  $R = 3.0$  a.u.  
All energies are in hartree a.u.

Cycle Number	Perturbation Theory	CCD		CCSD-1	
		[N,N-1],[N,N] Pade Approximants	Reduced Linear Equation	[N,N-1],[N,N] Pade Approximants	Reduced Linear Equation
1	-108.987225	-109.136925	-109.044716	-109.175100	-109.044716
2	-109.136720	.082456	.086632	1.099856	.105533
3	.051536	.085520	.085880	.104841	.107266
4	.108074	.089926	.095766	.111006	.115625
5	.075550	.091371	.090744	.112551	.112060
6	.097451	.091567	.092244	.112966	.113922
7	.085099	.092383	.091670	.113627	.113088
8	.093637	.091743	.091785	.113243	.113339
9	.088970	.091748	.091750	.113259	.113264
10	.092316	.091755	.091753	.113265	.113272
11	.090566	.091752		.113269	.113266
12	.091886	.091753		.113267	.113268
$\infty$	.091753			.113268	

**DATA  
FILM**